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Ferrocenyl-phosphonium ionic liquids – synthesis, characterisation and electrochemistry†

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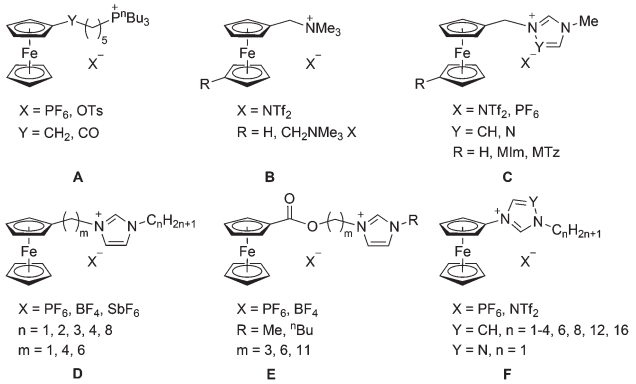
New unsymmetrically substituted ferrocenyl-phosphonium ionic liquids (ILs) $[FcPR_2R']NTf_2$ **5a–j** are synthesized by two or three step syntheses starting from ferrocene, Fc = $(C_5H_5)Fe(C_5H_4)$; R = Me, ^{n}Bu, ^{n}Hex, Ph; R' = Me, ^{n}Pr, ^{n}Bu, Ph; NTf_2 = $N(SO_2CF_3)_2$. The selective synthesis of alkyl phosphines $FcPR_2$ *via* a Friedel–Crafts phosphorylation is highlighted as an alternative for the standard protocol commonly used for ferrocenyl arylphosphines involving lithiation of FcH followed by phosphorylation. The influence of the P-substituents on thermal stability, electrochemical potential, chemical shift, and UV-Vis absorption behavior of the ILs is studied. The phosphonium group acts both as an ionic tag and as an electron-withdrawing substituent directly bound at the Cp-ring position. Therefore the title compounds are attractive for further studies to use them as tunable redox mediators for (photo)electrochemical devices such as dye sensitized solar cells (DSSCs) or redox flow batteries.

Introduction

In recent years a number of ferrocene based ionic liquids have been reported and their electrochemical properties have been examined (Scheme 1).

First applications for these redox-active compounds include surface structuring of precious metals[6] like platinum, silver and gold, electron transfer across the interface between two phases[7] as well as additives for lithium-ion batteries[8] to prevent overcharging/discharging. Furthermore, a ferrocene based supported ionic liquid phase (SILP) catalyst[9] has been used in a multi-component synthesis. Ionic liquids based on organosubstituted ferrocenium cations [FcR]X have been investigated, which however after reduction lose their ionic character and retention properties in electrolytes.[10] Furthermore low-melting heteroleptic sandwich compounds of the form $[(C_5H_4R)Fe(arene)]X$ came into focus[11] but they tend to be not robust enough against light.

In the field of ferrocenyl-phosphonium ILs only a few compounds of the form $[FcPR_3]X$ (R = alkyl, aryl; X = halide, BF_4) are known.[12] These are typically based on quaternized diphenylferrocenylphosphine (**2d**) which results in melting points between 175 °C and 222 °C. In rare cases the electrochemical properties have been studied (*e.g.* $[FcPPh_2Me]I$, $E_{1/2}$ = 1.01 V (*vs.* SCE in DCM)[13]). Probably due to the synthetic challenge the influence of a set of different alkyl groups at the phosphorus atom on the physical properties has not yet been investigated.



Scheme 1 Literature-known ferrocene based ionic liquids (**A**,[1] **B**,[2] **C**,[2] **D**,[3] **E**,[4] **F**[5]).

The synthetic access to diphenylphosphino derivative **2d** includes salt elimination[14] from *in situ* generated monolithioferrocene (FcLi) with Ph_2PCl (**1d**), the visible-light photolysis[15] of $[(C_5H_5)Fe(arene)]PF_6$ in the presence of $Li[C_5H_4PPh_2]$ or Friedel–Crafts phosphorylation[16] of ferrocene (FcH) with **1d**.

In the case of alkyl-substituted ferrocenylphosphines only salt elimination from *in situ* generated FcLi with R_2PCl has been described; however, with decreasing steric bulk of the alkyl group the yield is dropping strongly (R = ^{t}Bu (45–78%),[17] Cy (44–70%),[18] Et (30%),[19] Me (23%)[20]). Another disadvantage

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of this synthetic route is the necessary chromatographic separation of the obtained product mixture (FcH, $FcPR_2$, $Fc'(PR_2)_2$ ($Fc' = (C_5H_4)_2Fe$)) under an inert-gas atmosphere.

Here we present a selective synthesis of $FcPR_2$ (R = Me, ^{n}Bu, ^{n}Hex) *via* Friedel–Crafts phosphorylation of FcH with R_2PCl. Related phosphonium-ILs can either be prepared by alkylation with alkylhalides (MeI, ^{n}PrBr, ^{n}BuBr) and subsequent anion exchange or by direct alkylation with methyl bis(trifluoromethanesulfonyl)imide **6**.

Results and discussion

Synthesis of dialkylferrocenylphosphines 2a–c

The preparation of the dialkylchlorophosphines **1a–c**, required for the Friedel–Crafts phosphorylation, was implemented either by a literature-known, four-step synthesis[21] or *via* one-pot synthesis based on PCl_3. The method presented here proceeds from a direct alkylation of PCl_3 with organolithium compounds RLi (R = ^{n}Bu, ^{n}Hex). Slow addition of the pre-cooled (−78 °C) organolithium compounds is crucial to avoid undesired by-products ($RPCl_2$, R_3P, phosphinophosphonium compounds[22]).

We found that by variation of the reaction conditions the Friedel–Crafts phosphorylation of FcH with aromatic Ph_2PCl **1d**[16] can be also applied for dialkylchlorophosphines R_2PCl (R = Me, ^{n}Bu, ^{n}Hex). Based on ^{31}P NMR monitoring of the conversion of ferrocene with ^{n}Bu$_2$PCl **1b** and $AlCl_3$ a reaction pathway is proposed (Scheme 2).

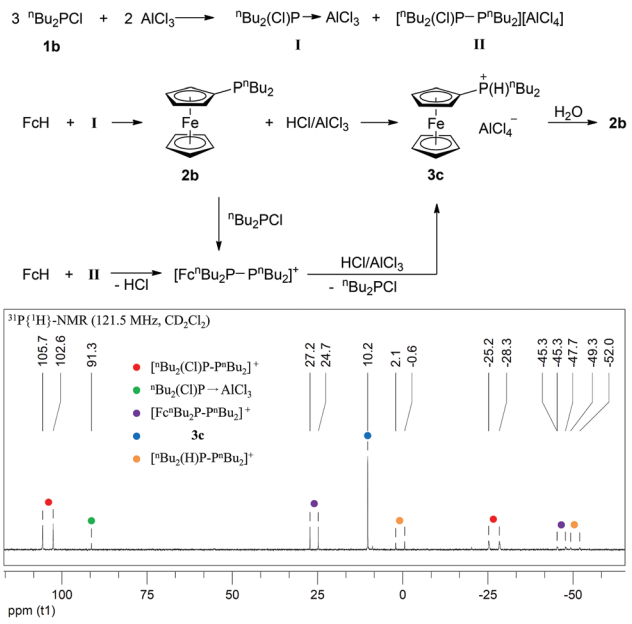
In the first step the Lewis acid $AlCl_3$ reacts with ^{n}Bu$_2$PCl **1b** yielding a mixture of the complex ^{n}Bu$_2$(Cl)P–$AlCl_3$ **I** and the tetrachloro-aluminate salt of the phosphinophosphonium cation [^{n}Bu$_2$(Cl)P–P^{n}Bu$_2$]$^+$ **II** under the prevailing conditions. This behavior has been described in the literature for a number of R_2PCl and several Lewis acids.[22] Nucleophilic attack of FcH at these positively charged phosphorus atoms under release of hydrogen chloride detected as a gaseous by-product and $AlCl_3$ yields the desired phosphine **2b**. This phosphine reacts with *in situ* generated HCl in the presence of $AlCl_3$ to [FcP(H)^{n}Bu$_2$]$AlCl_4$ **3c** which was isolated from the reaction mixture and characterized by NMR spectroscopy as well as mass spectrometry. The phosphine **2b** may also react with an excess of ^{n}Bu$_2$PCl **1b** to the phosphinophosphonium cation [Fc^{n}Bu$_2$P–P^{n}Bu$_2$]$^+$, which was independently confirmed by reaction of **2b**, **1b** and $AlCl_3$ in DCM displaying NMR signals $\delta_P(CD_2Cl_2)$ = 27.7; −45.3 ppm; $^1J_{PP}$ = 300.0 Hz. The cation [Fc^{n}Bu$_2$P–P^{n}Bu$_2$]$^+$ is converted to **3c** by reaction with *in situ* generated HCl/$AlCl_3$ and can be separated from the unreacted starting material (FcH, ^{n}Bu$_2$PCl) by washing with *n*-pentane. The cation [FcP(H)^{n}Bu$_2$]$^+$ is a weak acid (pK_{BH^+}(**3a**) = 7.51) which was determined by NMR titration of **2b** with [PhP(H)^{n}Bu$_2$]NTf_2 **3b** of literature-known pK_{BH^+};[24] thus **3c** can be deprotonated by degassed water yielding phosphine **2b** of high purity.[25]

In contrast to the selective Friedel–Crafts phosphorylation a product mixture was obtained during the reaction from *in situ* generated FcLi with Me_2PCl **1a**.[26]

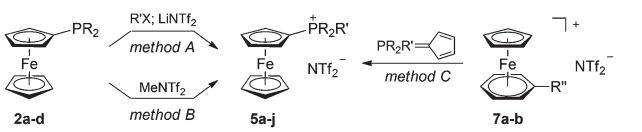
Synthesis of ferrocenyl-phosphonium ILs 5a–j

Different synthetic routes to phosphonium compounds **5a–j** are presented in Scheme 3 and received products in Table 1. Two of these strategies are based on the phosphines **2a–d** and differ only in the employed alkylating agents (*method A* and *B*). In *method C* the phosphonium moiety is inserted through a photolytic conversion of heteroleptic sandwich compounds of the form [(C_5H_5)Fe(arene)]NTf_2 with cyclopentadienylidene phosphoranes.

The very nucleophilic alkyl phosphines **2a–c** can be quaternized with any alkyl halides in high yields. However, the resulting phosphonium halides **4a–f** exhibit high melting points and a small electrochemical window. Therefore, *via* anion-metathesis with $LiNTf_2$ they are converted into the corresponding NTf_2 salts. The main drawback of this two-step synthesis is the anion-metathesis. In the case of incomplete conversion remaining redox-active halide ions or lithium halide would contaminate the product leading to an additional



Scheme 2 Proposed reaction mechanism (top); observed ^{31}P NMR spectrum of the reaction of FcH, ^{n}Bu$_2$PCl and $AlCl_3$ in CD_2Cl_2 after 1 h (bottom).[23]

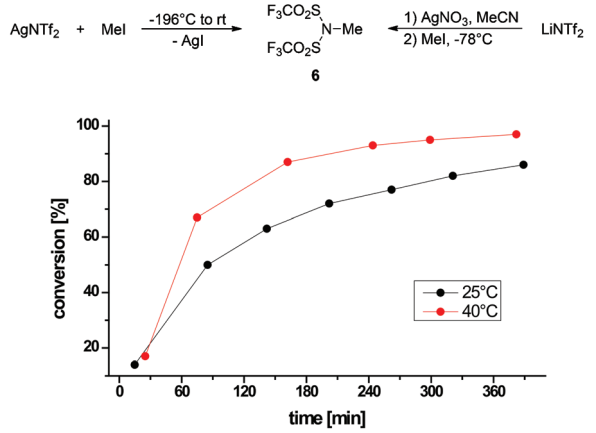


method A: R = R' = Me **5a**; R = Me, R' = ^{n}Pr **5b**; R = Me, R' = ^{n}Bu **5c**; R = ^{n}Bu, R' = Me **5d**; R = ^{n}Bu, R' = ^{n}Pr **5e**; R = R' = ^{n}Bu **5f**
method B: R' = Me; R = Me **5a**; R = ^{n}Bu **5d**; R = ^{n}Hex **5g**; R = Ph **5h**; Fc'$(PPh_2Me)_2$ **5j**
method C: R = R' = ^{n}Bu **5f**; R = R' = Ph **5i**; R": H, Me

Scheme 3 Synthetic routes to **5a–j**; *method A*: (1) R'X, MeCN; (2) $LiNTf_2$, MeOH–H_2O; *method B*: $MeNTf_2$, MeCN; *method C*: $CpPR_2R'$ (R = R' = Ph **8a**, R = R' = ^{n}Bu **8b**), MeCN, $h\nu$.

Table 1 Compound numbering for [$FcPR_2R'$]X

$FcPR_2$	R′	Anion [X]
$FcPMe_2$ **2a**	Me	I **4a**, NTf_2 **5a**
	^{n}Pr	Br **4b**, NTf_2 **5b**
	^{n}Bu	Br **4c**, NTf_2 **5c**
FcP^nBu_2 **2b**	H	NTf_2 **3a**, $AlCl_4$ **3c**
	Me	I **4d**, NTf_2 **5d**
	^{n}Pr	Br **4e**, NTf_2 **5e**
	^{n}Bu	Br **4f**, NTf_2 **5f**
FcP^nHex_2 **2c**	Me	NTf_2 **5g**
$FcPPh_2$ **2d**	Me	NTf_2 **5h**
	Ph	NTf_2 **5i**
$Fc'(PPh_2)_2$	Me	NTf_2 **5j**



Scheme 4 Synthetic approach for $MeNTf_2$ (top); methylation of FcP^nBu_2 **2b** with $MeNTf_2$ **6** in $CDCl_3$ at various temperatures. The reaction progress was monitored by ^{31}P NMR spectroscopy (bottom).

expenditure in purifying the redox-active IL up to electrochemical grade. Furthermore, the resulting product has to be dried under high-vacuum for an extended period of time in order to remove traces of water.

For these reasons the strategy was varied in order to obtain the desired IL by direct alkylation with $MeNTf_2$ **6** in one step. **6** is literature-known, but so far only its application as an alkylating agent has been described.[27] To the best of our knowledge, no synthetic procedure for **6** is given in the literature; therefore, we present two possible syntheses (Scheme 4). Both are based on a salt elimination reaction of $AgNTf_2$ with MeI. In the first case $AgNTf_2$ is prepared by a literature-known[28] synthesis of $HNTf_2$ with Ag_2O, subsequently isolated and further implemented. An additional possibility is the reaction of $LiNTf_2$ with $AgNO_3$ in MeCN, forming the room temperature ionic liquid (RTIL) $[Ag(MeCN)_4]_2[Ag(NTf_2)_3]$.[29] From this compound $MeNTf_2$ **6** can be prepared by reaction with MeI followed by removal of surplus MeCN by distillation. Alternatively, MeCN can be removed under vacuum (120 °C/0.02 mbar) to form solvent-free $AgNTf_2$ prior reaction with MeI.[30]

A reactivity study showed that $MeNTf_2$ is not such a powerful methylating agent as MeI or Me_2SO_4, respectively: while reaction of **2b** with MeI or Me_2SO_4 in $CDCl_3$ at 25 °C proceeds spontaneously, it was possible to monitor the conversion at 25 °C and 40 °C by ^{31}P NMR spectroscopy in the case of $MeNTf_2$ (Scheme 4).

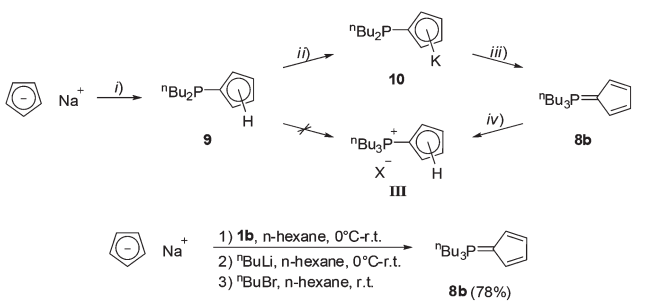
Nevertheless, all phosphines **2a–d** could selectively be methylated with **6**, and pure ionic liquids **5a**, **5d**, **5g** and **5h** were obtained directly. Furthermore it was possible to methylate dppf at both phosphorus atoms with 2.0 eq. of **6**. However, due to its lower nucleophilicity and poor solubility of dppf and its monoalkylated intermediate in MeCN the alkylation took 4 d (78% yield).

An alternative strategy for the preparation of ferrocenylphosphonium ILs is the visible-light photolysis of $[(C_5H_5)Fe(arene)]NTf_2$ with cyclopentadienylidene phosphoranes **8a–b**. While phenylphosphorane **8a** is literature-known,[31] alkylphosphoranes such as **8b** can be obtained from cyclopentadienyl substituted phosphines in straightforward protocols either by deprotonation of the related phosphonium halides[32] or *via* reaction of cyclopentadienides with alkyl halides[33] (Scheme 5).

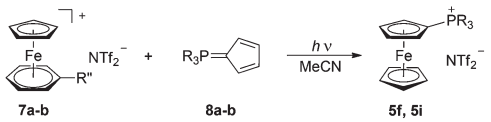
The self-evident quaternization of dibutylcyclopentadienyl phosphine **9** with 1-bromobutane turned out to be unselective. An observed side reaction proven by ESI-HRMS is the dimerization by the Diels–Alder addition of the two dienes.[34] However, reaction of potassium dibutylphosphinocyclopentadienide **10** with 1-bromobutane was directly leading to the new phosphorane **8b** (Scheme 5). Finally a straightforward one-pot synthesis based on sodium cyclopentadienide gave **8b** in 78% yield (Scheme 5, bottom). **8b** will turn out to be a very nice synthon for the preparation of zwitterionic and soluble metal complexes in general.

The photolysis of $[(C_5H_5)Fe(arene)]PF_6$ with substituted cyclopentadienide salts is literature-known and delivers in high yield functionalized ferrocenes.[15] Here we present the implementation of this promising method on the use of cyclopentadienylidene phosphoranes. Visible light photolysis (Osram Ultra Vitalux 300W) of $[(C_5H_5)Fe(arene)]NTf_2$ with **8a** and **8b** in MeCN proceeds readily to give the expected ferrocenyl-phosphonium ILs in quantitative yields. In this way, **5i** is available, which is not accessible *via* quaternization of **2d** (Scheme 6).

All phosphonium compounds **4a–g** and **5a–j** are soluble in polar organic solvents (DCM, THF, MeCN, MeOH, *etc.*) but



Scheme 5 Step by step reaction to **8b**; (i) ^{n}Bu_2PCl, *n*-pentane, 0 °C; (ii) benzyl potassium, Et_2O, 0 °C; (iii) ^{n}BuBr, Et_2O, r.t.; (iv) $HCl_{(g)}$, $CDCl_3$ (top); one-pot synthesis of **8b** (bottom).



7a-b 8a-b 5f, 5i

Scheme 6 Photolysis of $[(C_5H_5)Fe(arene)]NTf_2$ **7a–b** with cyclopentadienylidene phosphoranes **8a–b**. R = Ph, ^{n}Bu, R'' = H, Me.

insoluble in water and nonpolar organic solvents like toluene, Et_2O and hydrocarbons.[35] While the halides **4** were obtained as amorphous solids, the ionic liquids **5** reveal either a honey-like consistency (**5b**, **5e**) or are isolated as a wax (**5a**, **5c**, **5d**). The only exception is **5f** which was obtained as a solid. In addition, all NTf_2 salts are insensitive to oxygen and moisture in the air, which was determined by NMR spectroscopy over a period of five months.

Melting points and glass-transition temperatures

The melting points of most of the halides are in the range from 106.7 °C (**4e**) to 155.0 °C (**4c**). Exceptions are **4a** (T_m = 276.9 °C) and **4d** (glassy undercooled melt at r.t.). Interestingly, the trend in melting points for methyl derivative **4a** (276.9 °C) ≫ *n*-butyl derivative **4c** (155.0 °C) > *n*-propyl derivative **4b** (125.6 °C) is also found in the corresponding phenyl phosphonium halides [$PhPMe_2R$]X (R = Me, T_m: 238.9 °C;[36] R = ^{n}Pr, T_m: 118 °C;[37] R = ^{n}Bu, T_m: 132 °C[38]).

The conversion of the halide salts **4** into the NTf_2 salts **5** results in a decrease of the melting points. However an exact trend cannot be described since most of the compounds were obtained as glassy undercooled melts and no melting point could be determined by DSC.

The thermal stability of phosphonium compounds is generally very high and can be increased by substitution of the halides by weakly nucleophilic NTf_2.[39] This trend can also be observed for the trisalkylferrocenyl-phosphonium compounds discussed here. For the halides **4a–f** all decomposition temperatures T_d are below 300 °C and for the NTf_2 salts **5a–f** significantly higher than 300 °C (Table 2).

Spectroscopic properties

NMR spectroscopy. The ^{31}P and ^{1}H NMR spectra of the phosphines **2a–c** show a small influence of the length of the alkyl chain on the chemical shift of the respective phosphorus

Table 2 Phase transition and thermal decomposition temperatures

Compd	T_m [a]/°C	T_d [a]/°C	Compd	T_m (T_g)[c]/°C	T_d [d]/°C
4a	276.9	299.7	**5a**	—[b] (−30.6)	353.4
4b	125.6	200.4	**5b**	40.3 (−41.7)	356.1
4c	155.0	217.2	**5c**	—[b] (−42.0)	361.4
4d	—[b]	—[b]	**5d**	—[b] (−38.6)	359.1
4e	106.7	245.2	**5e**	43.7 (−41.5)	343.7
4f	129.3	268.7	**5f**	72.4 (—[e])	329.8

[a] Optical melting point determination. [b] Not measurable due to glassy undercooled melt. [c] Measured by differential scanning calorimetry. [d] T_d was recorded as the 5% weight loss temperature. [e] Not measured.

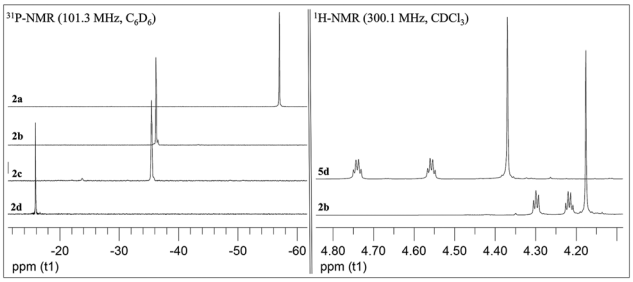


Fig. 1 ^{31}P NMR spectra of **2a–d** (left); ^{1}H NMR changes in chemical shift for α, β and C_5H_5 positions of **2b** and **5d**, respectively (right).

atoms and protons of the Cp-rings. This might be explained by the increasing electron-donating character with increasing length of the alkyl chain. In comparison with **2d** there is a stronger downfield shift due to the significantly stronger electron-donating property of the phenyl groups (δ_P(**2a**) ≪ δ_P(**2b**) < δ_P(**2c**) ≪ δ_P(**2d**); Fig. 1, left side).

By alkylation of the phosphorus atoms the electron-donating phosphine moieties are converted into electron-withdrawing phosphonium groups, which can be related to the electrochemical potential and to strong downfield shifts in the ^{31}P NMR ($\Delta\delta_P$(**2a** *vs.* **5b**) = 83.9 ppm; $\Delta\delta_P$(**2b** *vs.* **5e**) = 68.0 ppm). The same deshielding effect can be observed in the corresponding ^{1}H NMR spectrum (Fig. 1, right side). This is in accordance with former studies on substituent effects on chemical shifts in monosubstituted ferrocenes.[40]

UV-Vis spectroscopy. If these redox-active electrolytes are thought to be used as redox mediators in dye-sensitised solar cells, they should not have strong absorption bands in the visible light. As expected the absorption and extinction coefficient of each phosphonium compound is in the range of ferrocene (λ_{FcH} = 225 nm (ε = 5250 M^{-1} cm^{-1}) in EtOH).[41] In this regard the alkyl-substituted Fc-phosphonium IL **5d**, $\lambda_{\mathbf{5d}}$ = 259 nm (ε = 4481 M^{-1} cm^{-1}), has a much lower extinction coefficient than the phenyl-substituted ferrocenyl-phosphonium ILs **5h** and **5i**: $\lambda_{\mathbf{5h}}$ = 261 nm (ε = 6281 M^{-1} cm^{-1}); $\lambda_{\mathbf{5i}}$ = 261 nm (ε = 6499 M^{-1} cm^{-1}). In the visible region all three compounds show very low extinction coefficients (Table 3). In addition to the main absorption around 260 nm and the minor absorption in the visible light region, phenyl phosphonium salt **5i** shows a third absorption maximum at $\lambda_{\mathbf{5i}}$ = 308 nm with an extinction coefficient of ε = 1628 M^{-1} cm^{-1}.

Comparing these results with the absorption properties of [Me_4N][I_3], it can be seen that ferrocenyl-phosphonium ionic liquids have an up to ten times lower extinction coefficient in the near UV region and over a hundred times lower in the visible light region than the I^-/I_3^- redox couple often used in DSSCs[42] (Fig. 2). They do not compete that much for light absorbance.

Cyclic voltammetry. It is well-known that different substituents at the ferrocene backbone result in an alteration of its electrochemical potential.[43] The potential gets more negative by introducing electron-donating groups and more positive by electron withdrawing groups.[44] The electron-withdrawing character of different phosphonium groups leads to a more or less

Table 3 Selected absorption characteristics

Compd	λ_{max}/nm	ε/M^{-1} cm^{-1}	λ_{max}/nm	ε/M^{-1} cm^{-1}
5d[a]	259	4481	450	[c]
5h[a]	261	6281	447	241
5i[a]	261	6499	447	230
$[Me_4N][I_3]$[b]	292	45 800	362	25 000

[a] Measured in DCM. [b] Measured in 1,2-dichloroethane (see ref. 42). [c] Not determined.

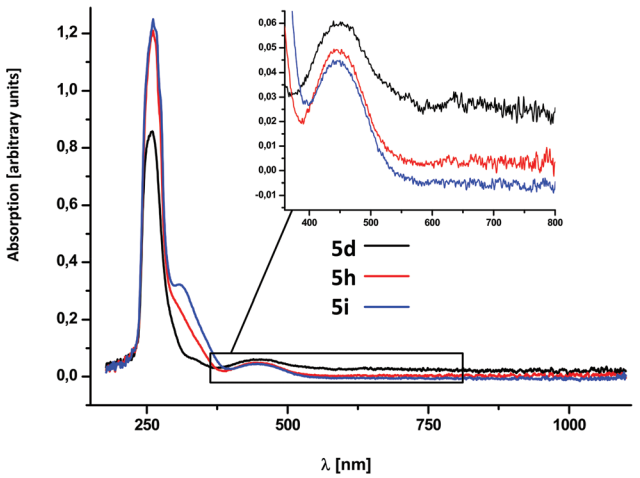


Fig. 2 UV-Vis spectra obtained from 0.2 mM solution of **5d**, **5h** and **5i** in DCM; inset shows spectral range of the visible spectrum.

positive equilibrium potential *vs.* FcH for all the ferrocenyl-phosphonium ILs **5a–j**.

As shown in Table 4 and Fig. 3 the potential shift is higher in case two phenylphosphonium groups are attached to ferrocene (**5j**), while it is lower with one alkylphosphonium group and lowest if an alkyl spacer is inserted between the Cp moiety and the phosphonium group, *e.g.* in **11**. In this respect the potential can be tuned.

CV measurements also allow one to control the purity of the products, *e.g.* the CV of **5j** shows very small redox waves next to the reversible redox process at $E_{1/2}$ (**5j**) = 983 mV attributable to a trace contamination of monoalkylated dppf, which independently was detected by ESI-HRMS. Due to the presence of the two lone pairs of electrons an electrochemical dimerization during the CV measurement has been discussed for dppf.[45] Similar reactions can be assumed for the monoalkylated dppf.

The electrochemical stability of the alkyl-substituted compounds was confirmed by a measurement of neat **5e** at 60 °C.

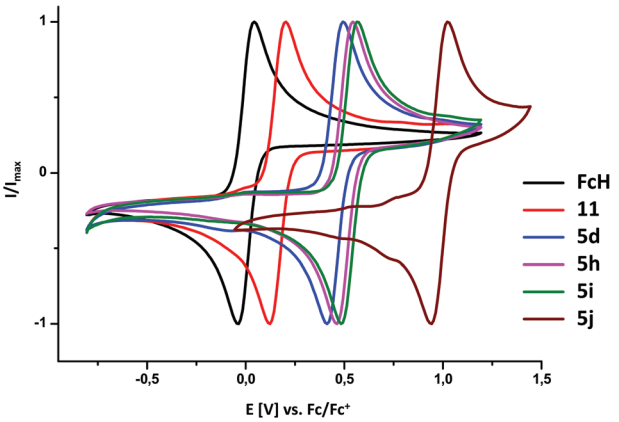


Fig. 3 CV scans for some ferrocenyl-phosphonium compounds in comparison with ferrocene; approx. 5 mM in [EMIM]NTf$_2$ at 50 mV s^{-1} *vs.* Ag/AgNTf$_2$ as a reference electrode; **11**: [FcCHMePBu$_3$]NTf$_2$.

5e has a reversible stability from −2.45 V to 2.10 V, which corresponds to a remarkable chemical window of 4.55 V. The chemical window of **11** (−2.45 V to 1.81 V) is a little bit smaller due to the predetermined P–C bond cleavage at the alkylene spacer forming the privileged cation [FcCHMe]$^+$ which was also proven by ESI-HRMS.

Crystal structures. Single-crystal analyses could be obtained for **4a** and **5f** either from a saturated chloroform solution or by slow diffusion of Et$_2$O into an acetonitrile solution.

Crystallographic data are listed in Table 6, selected bond distances and angles are shown in Table 5, and for comparison, the corresponding data for two closely related salts, [FcPPh$_2$(CH$_2$Ph)]Cl[12] **VII** and [FcPPh$_2$(CH$_2$C$_6$H$_4$OMe)]BF$_4$ [48] **VIII**, are also included. Full details are available *via* ESI.†

5g crystallizes monoclinic ($P2_1/c$), while crystals of **4a** are cubic ($Pa\bar{3}$). The packing of **4a** shows weak C–H···I contacts with a minimum distance of 311.4 pm, which is lower than the sum of the van der Waals radii of 335 pm.[46] The P···I distances vary from 480.0 pm to 800.0 pm. Similar to other quaternary phosphonium salts, there is no direct P···I anion cation interaction.[36,47]

Phosphorus–alkyl bond distances for both compounds are approximately constant (**4a**: 177.2 ± 0.5 pm; **5f**: 179.7 ± 0.5 pm) and a bit shorter than the average value of 184 pm reported for the P–C(sp^3) bond.[49] The same situation is found for the P–C$_{Cp}$ bond distances (176.4 and 177.2 pm for **4a** and **5f**, respectively).

These are larger in comparison with cyclopentadienylidene phosphoranes (C$_5$H$_4$PPh$_2$Me:[32] 172.7 pm; C$_5$H$_4$PPh$_3$:[50] 171.8 pm; Cp^{TM}PPh$_2$Me:[33] 171.4 pm). In η^5-coordinated

Table 4 Cyclic voltammetry of ferrocenyl-phosphonium compounds[a]

Compound	5a	5b	5c	5d	5e	5f	5g	5h	5i	5j	11
E [mV] *vs.* Fc/Fc$^+$	458	458	463	454	453	454	453	504	523	983	164

[a] Approx. 5 mM in [EMIM]NTf$_2$ at 50 mV s^{-1} *vs.* Ag/AgNTf$_2$ as a reference electrode.

Table 5 Selected bond distances (pm) and angles (°) for **4a**, **5f** and related compounds [$FcPPh_2(CH_2Ph)$]Cl (**VII**) and [$FcPPh_2(CH_2C_6H_4OMe)$]-BF_4 (**VIII**)

	4a	5f	VII[a]	VIII[a]
C_{Cp}–P	176.4(6)	177.2(3)	176.7(5)	177.9(4)
C_{alkyl}–P	177.0(6)	180.1(4)	181.9(5)	181.3(4)
	176.7(4)	179.2(3)		
	177.7(6)	180.2(3)		
C_{Cp}–C_{Cp}	144.3(8)	142.6(5)	143.2(3)	142.8(6)
	142.6(8)	141.1(6)	142.6(4)	141.8(6)
	142.3(9)	141.0(6)	140.6(3)	141.6(8)
	142.2(9)	141.6(6)	141.8(4)	140.9(6)
	141.6(9)	143.9(5)	145.3(4)	142.3(7)
$C_{Cp'}$–$C_{Cp'}$	142.6(9)	141.1(6)	140.1(3)	137.6(8)
	143.0(9)	141.4(6)	141.5(4)	137.3(8)
	141.1(9)	140.2(6)	137.4(3)	137.8(11)
	139.1(9)	139.8(6)	138.0(3)	139.6(8)
	142.5(9)	142.5(6)	138.4(4)	138.1(9)
$C_{Cp,i}$–Fe	163.7(1)	164.3(1)	164.5(4)	164.5(2)
$C_{Cp',i}$–Fe	165.5(1)	164.9(1)	165.9(4)	166.3(2)
$C_{Cp,i}$–Fe–$C_{Cp',i}$	174.2(6)	174.2(3)	174.9(2)	176.3(1)
$C_{Cp,i}$–C_{Cp}–P	176.0(5)	172.9(2)	175.2(1)	175.5(3)
C_{Cp}–P–C_{alkyl}	110.3(3)	106.7(2)	111.6(1)	108.0(2)
	110.7(3)	111.2(1)		
	109.1(3)	111.5(1)		
C_{alkyl}–P–C_{alkyl}	107.2(3)	109.1(2)		
	108.2(3)	107.3(2)		
	111.3(3)	110.9(2)		

[a] **VII**: see ref. 12, **VIII**: see ref. 48.

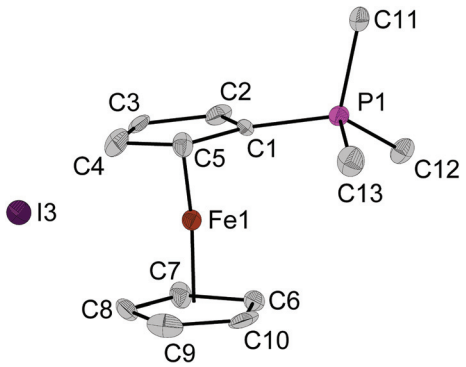


Fig. 4 Molecular structure of **4a**. Displacement ellipsoids are shown for 50% probability, hydrogen atoms are omitted for clarity; the four iodide ions present in the unit cell are symmetry independent, and therefore cannot be distinguished. For clarity, only one iodide ion is displayed.

cyclopentadienylidene phosphoranes much less negative charge is delocalized into empty orbitals of the phosphonio group than in non-coordinated ones. As a consequence no significant P–C_{Cp} bond shortening and no C_{Cp}–C_{Cp} bond length alteration (**4a**: 142.6 ± 1 pm; **5f**: 142.0 ± 1 pm) is observed in the η^5-coordinated cyclopentadienyl units (Fig. 4 and 5).

Interestingly, despite steric aspects the distances of the iron atom to the centroid of the phosphonio-substituted Cp rings (**4a**: 163.7 pm; **5f**: 164.3 pm) are shorter compared to the unsubstituted Cp rings (**4a**: 165.5 pm; **5f**: 164.9 pm). The dihedral angle between the planes of the two Cp rings is 5.3° for

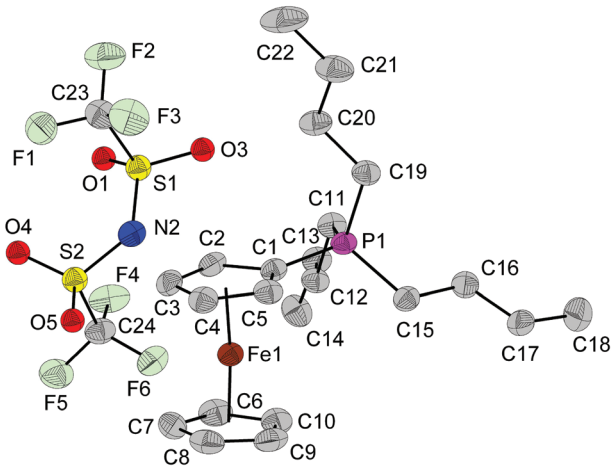


Fig. 5 Molecular structure of **5f**. Displacement ellipsoids are shown for 50% probability, hydrogen atoms are omitted for clarity.

4a and 5.5° for **5f**, which is slightly higher than for the known compounds (**VII**: 4.7°; **VIII**: 3.6°). Both phosphorus atoms are displaced 13.3 pm and 21.0 pm (for **4a** and **5f**, respectively) out of the plane defined by the Cp rings.

For the literature-known compounds **VII** (deviation: 2.3°) and **VIII** (deviation: 4.0°) a nearly perfect eclipsed structure for the arrangement of the Cp rings is found. For the new compounds the same trend is observed, but the deviation is higher (9.4°) for **4a** and smaller (0.1°) for **5f**.

Conclusions

A new series of unsymmetrically substituted trisalkylferrocenylphosphonium ILs were prepared by various synthetic strategies using cheap starting materials. For this purpose a selective Friedel–Crafts phosphorylation in the preparation of dialkylferrocenylphosphines has been established as a more selective alternative to FcH lithiation and subsequent reaction with R_2PCl. Furthermore, the purity of the desired phosphonium ILs has been increased and the number of synthetic steps could be reduced by the use of $MeNTf_2$ as an alkylating agent. A simple synthesis for $MeNTf_2$ based on commercially available $LiNTf_2$ has been described. Another synthon useful for many further studies, the new tributyl-cyclopentadienylidene phosphorane **8b**, has been obtained in a simple one-pot synthesis.

The influence of the substituents at the phosphorus atom on the thermal stability, the electrochemical potential, the melting points as well as the absorption behavior has been investigated. Generally all phosphonio-substituted ferrocenes showed a shift to more positive potentials, as phosphonium groups are electron-withdrawing substituents. This tunable redox potential and low absorption coefficients make these new compounds attractive for the use as redox mediators in dye sensitized solar cells (DSSCs). Due to the fact that the overall efficiency of the cell is proportional to the open circuit

voltage[51] (V_{OC}), a lowering of the potential of the redox mediator leads to an increase of V_{OC}.

Experimental

General remarks

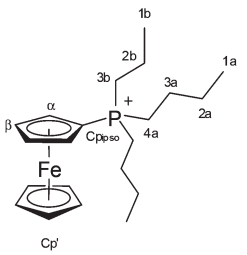
Synthesis and handling of air- and moisture-sensitive substances was carried out using standard Schlenk- and glovebox-techniques. Solvents were dried using standard procedures[52] and stored over an Al_2O_3/molecular sieve 3 Å/R3-11G catalyst (BASF).

The following starting materials were prepared according to literature procedures: dimethylchlorophosphine (**1a**),[21] diphenylferrocenylphosphine (**2d**),[16] 1,1′-bis(diphenylphosphino)-ferrocene (dppf),[14] silver bis(trifluoromethanesulfonyl)imide ($AgNTf_2$),[28] bis(trifluoromethanesulfonyl)amine ($HNTf_2$),[28] sodium cyclopentadienide (NaCp),[53] triphenylcyclopentadienylidene phosphorane ($CpPPh_3$),[54] $[(C_5H_5)Fe(\eta^6\text{-toluene})]NTf_2$,[55] benzyl potassium (BzK),[56] dibutylphenylphosphine,[57] 1-hydroxyethylferrocene (FcCHMeOH),[58] tributylphosphine hydrobromide.[59] $AlCl_3$ (98%, Merck) was sublimated, 1-bromobutane (99%, Acros Organics) was dried over calcium hydride and purified by vacuum distillation before use. $[EMIM]NTf_2$ (electrochemical grade, IoLiTec) was degassed and dried in a vacuum at 60 °C/3 × 10^{-5} mbar. Other starting materials were obtained from commercial sources (Sigma-Aldrich, Merck, Acros Organics) and used as received. All reactions involving silver salts were carried out under exclusion of light.

NMR spectra were recorded at 300 K on a Bruker AC 300, DRX 400 or DRX 500 using CD_3CN, $CDCl_3$, CD_2Cl_2, C_6D_6 or THF-d_8 as solvent. Chemical shifts are given with respect to tetramethylsilane (^1H, ^{13}C), phosphoric acid (^{31}P) and $CFCl_3$ (^{19}F), respectively. Calibration of ^1H and ^{13}C NMR spectra was accomplished with the solvent signals; ^{31}P and ^{19}F NMR spectra were calibrated externally unless otherwise specified.

The applied numbering scheme is shown beneath. If no assignment was possible for the resonances of positions α and β, they are mentioned with H_{Cp} or C_{Cp}, respectively (Scheme 7).

ESI and APCI mass spectra were recorded on a Thermo Fisher Scientific LTQ FT Ultra using methanol or dichloromethane as solvents. EI mass spectra were recorded on a Finnigan MAT95. The *m*/*z* values are given together with their relative intensities. Isotopic patterns were in all cases consistent with natural abundance.



Scheme 7 Example of numbering of compounds.

IR spectra were recorded on a Bruker Alpha FT-IR spectrometer using neat samples with an ATR measurement setup (diamond cell) at room temperature.

Elemental analysis was done on an Elementar vario MICRO cube. Values are given in weight percent. In the case of the prepared phosphines elemental analysis was not possible due to high sensitivity; thus, the purity of the compounds is demonstrated by NMR spectroscopy and high resolution EI spectrometry (see ESI†).

UV-Vis spectra were taken on an Avantes AvaSpec-2048 spectrophotometer at room temperature. All measurements were carried out in a glovebox.

Melting points (T_m or T_g) were measured by differential scanning calorimetry (DSC) using a Mettler Toledo DSC 821e calorimeter with a heating rate of 10 °C min^{-1} or *via* optical melting point determination using a Büchi melting point B-540 with a heating rate of 10 °C min^{-1}. Thermogravimetric analysis (TGA) was performed using a Mettler Toledo TGA/SDTA 851e apparatus between 25 and 800 °C; the heating rate was 10 °C min^{-1}.

Cyclic voltammetry (CV) experiments were performed using a RHD Instruments Microcell HC and an Ivium Technologies Iviumstat in a glovebox (N_2-atmosphere, O_2 and water content below 2 ppm and 1 ppm respectively). Experiments were performed at ambient temperature (25.0 °C) with an analyte concentration of 4.5–7.5 mM in $[EMIM]NTf_2$ as the supporting electrolyte unless otherwise specified. A three-electrode setup was used, where a ∅ = 0.25 mm Pt-wire was used as a working electrode and a 70 µl platinum crucible acted as a sample container as well as a counter electrode. Both were polished with Kemet diamond paste 0.25 µm direct prior to measurements. The reference electrode was 100 mM $Ag/AgNTf_2$ in $[EMIM]NTf_2$.[60] The reference electrode potential was determined with a ferrocene solution (6.22 mM in $[EMIM]NTf_2$) prior to and after measurement. Data were collected at 50 mV s^{-1} unless otherwise specified.

Table 6 Crystallographic data

	4a	**5f**
Chemical formula	$C_{13}H_{18}FeIP$	$C_{24}H_{36}F_6FeNO_4PS_2$
M/g mol^{-1}	388.01	667.11
Crystal system	Cubic	Monoclinic
Space group	$Pa\bar{3}$	$P2_1/c$
a/Å	20.3608(13)	10.6934(3)
b/Å	20.3608(13)	14.4249(6)
c/Å	20.3608(13)	20.1051(7)
α/°	90	90
β/°	90	97.508(3)
γ /°	90	90
V/Å^3	8440.8(9)	3074.65(19)
T/K	100(2)	100(2)
Z	24	4
No. reflections measured	7968	23 096
No. independent reflections	2978	6538
R_{int}	0.0941	0.1064
Final R_1 values ($I > 2\sigma(I)$)	0.0296	0.0568
Final w$R(F^2)$ values (all data)	0.0417	0.1411

Crystallographic data are provided in Table 6 and full details are available in ESI.† X-Ray data collection was performed *via* a STOE IPDS I or IPDS II area detector using Mo-K_α-radiation (λ = 71.073 pm). STOE IPDS software[61] was used for integration and data reduction; structure solution and refinement was done with the WinGX program suite[62] using SIR92[63] and SHELX-97.[64]

Synthesis of compounds

Preparation of dibutylchlorophosphine (1b) (^{n}Bu$_2$PCl). *Method A*: 5.00 g Mg-powder (0.21 mol, 3.3 eq.) was activated by heating in a vacuum and afterwards suspended in 60 mL Et_2O. To this suspension 30.14 g 1-bromobutane (0.22 mol, 3.5 eq.) in 30 mL Et_2O was slowly added until the solvent started boiling. The mixture was heated to reflux for 2.5 h. At 0 °C 10.75 g thiophosphoryl chloride (63.45 mmol, 1.0 eq.) in 15 mL Et_2O was added dropwise and after complete addition heated to reflux for 1 h. The reaction mixture was brought to ambient temperature and poured slowly into 150 mL ice water. The aqueous phase was acidified with hydrochloric acid and extracted five times with 50 mL Et_2O. The combined ether phases were dried over $MgSO_4$, filtered and after removing the solvent in a vacuum 11.02 g tetrabutyldiphosphine disulfide (31.09 mmol) was received as a slightly yellow solid. The yellow solid was redissolved in 20 mL benzene. 8.39 g sulfuryl chloride (62.18 mmol, 0.98 eq.) in 10 mL benzene was slowly added at 0 °C. After addition the reaction mixture was stirred for 12 h at ambient temperature and the solvent was removed by distillation under ambient pressure. The residue was distilled at 145 °C/1 mbar to get 10.32 g dibutylthiophosphinyl chloride (48.50 mmol) as a brown liquid. 10.32 g dibutylthiophosphinyl chloride (48.50 mmol, 0.76 eq.) and 15.27 g PPh_3 (58.2 mmol, 0.92 eq.) were heated for 1 d at 140 °C and subsequent distillation at 150 °C/1 mbar gave 8.06 g **1b** (44.62 mmol, 70%) as a colorless liquid. *Method B*: 13.65 g phosphorus trichloride (99.40 mmol, 1.0 eq.) was dissolved in 500 mL *n*-pentane and cooled to −78 °C. A cooled (−78 °C) solution of 63.7 mL *n*-butyllithium (1.60 M in *n*-hexane, 99.40 mmol, 1.0 eq.) dissolved in 100 mL *n*-pentane was added dropwise over a period of 105 min. The resulting suspension was stirred for 1 h at −78 °C and a second equivalent *n*-butyllithium (63.7 mL, 99.40 mmol, 1.0 eq.) dissolved in 100 mL *n*-pentane and cooled to −78 °C was slowly added over a period of 105 min. The reaction mixture was stirred over 24 h at −55 °C. The suspension was filtered at −30 °C over Celite® and washed two times with 60 mL *n*-pentane. The *n*-pentane was removed by distillation under ambient pressure yielding a yellow suspension. The crude product was distilled at 54 °C/0.02 mbar to obtain 7.70 g **1b** (42.60 mmol, 43%). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6) δ = 112.9 ppm; ^1H NMR (300.1 MHz, C_6D_6) δ = 0.79 (t, 6H, $^3J_{HH}$ = 7.3 Hz, $P(CH_2)_3\mathit{Me}$), 1.17–1.31 (m, 4H, $P(CH_2)_2CH_2Me$), 1.36–1.50 (m, 4H, PCH_2CH_2Et), 1.51–1.72 (m, 4H, $PCH_2{}^nPr$) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6) δ = 13.9 (s, $P(CH_2)_3\mathit{Me}$), 24.2 (d, $^3J_{CP}$ = 10.8 Hz, $P(CH_2)_2CH_2Me$), 27.0 (d, $^2J_{CP}$ = 13.0 Hz, PCH_2CH_2Et), 35.1 (d, $^1J_{CP}$ = 29.7 Hz, $PCH_2{}^nPr$) ppm.

Preparation of dihexylchlorophosphine (1c) (^{n}Hex$_2$PCl). 17.42 g phosphorus trichloride (0.13 mol, 1.0 eq.) was dissolved in 500 mL *n*-pentane and cooled to −78 °C. A cooled (−78 °C) solution of 47.4 mL *n*-hexyllithium (2.68 M in *n*-hexane, 0.13 mol, 1.0 eq.) dissolved in 100 mL *n*-pentane was added dropwise over a period of 80 min. The resulting suspension was stirred for 2 h at −78 °C and a second equivalent *n*-hexyllithium (47.4 mL, 0.13 mol, 1.0 eq.) dissolved in 100 mL *n*-pentane and cooled to −78 °C was slowly added over a period of 3 h. The reaction mixture was stirred over 15 h whereby the solution warmed up to −64 °C. A reaction control *via* ^{31}P NMR spectroscopy presented an 87% conversion for which reason additional *n*-hexyllithium (6.16 mL, 16.51 mmol, 0.13 eq.) was added over 15 min. After stirring for 1 h *n*-pentane was removed at 60 °C/ambient pressure and the resulting residue was recondensed at 130 °C/0.02 mbar to obtain the crude product (21.97 g, 92.79 mmol, 73%) as a slightly yellow liquid. To receive **1c** (16.90 g, 71.39 mmol, 56%) distillation at 150 °C/0.1 mbar has been implemented. $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6) δ = 113.6 ppm; ^1H NMR (300.1 MHz, C_6D_6) δ = 0.86 (t, 6H, $^3J_{HH}$ = 7.0 Hz, $P(CH_2)_5\mathit{Me}$), 1.09–1.30 (m, 12H, $P(CH_2)_4CH_2Me$, $P(CH_2)_3CH_2Et$, $P(CH_2)_2CH_2{}^nPr$), 1.43–1.53 (m, 4H, $PCH_2CH_2{}^nBu$), 1.55–1.65 (m, 4H, $PCH_2{}^nPent$) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6) δ = 14.2 (s, $P(CH_2)_5\mathit{Me}$), 22.9 (s, $P(CH_2)_4CH_2Me$), 24.9 (d, $^2J_{CP}$ = 13.1 Hz, $PCH_2CH_2{}^nBu$), 30.8 (d, $^3J_{CP}$ = 10.5 Hz, $P(CH_2)_2CH_2{}^nPr$), 31.8 (s, $P(CH_2)_3CH_2Et$), 35.5 (d, $^1J_{CP}$ = 29.8 Hz, $PCH_2{}^nPent$) ppm.

General procedure for the preparation of 2

Ferrocene (1.0 eq.) and $AlCl_3$ (1.1–1.2 eq.) were suspended in a sufficient amount of *n*-hexane (5 mL mmol^{-1} ferrocene). The appropriate dialkylchlorophosphine **1** (1.0–1.2 eq.) was added *via* a syringe and the reaction mixture was heated to reflux for 12 h whereupon a dark green oil was formed. The oil was washed with *n*-hexane several times until unreacted starting materials had been separated. The oil was suspended in 20 mL *n*-pentane and 20 mL degassed H_2O was added. After vigorous stirring the orange discolored organic phase was separated and the aqueous solution was extracted with *n*-pentane until no coloration could be obtained. The solvent of the combined organic phases was removed in a vacuum yielding the desired phosphine as a red oil.

Dimethylferrocenylphosphine (2a) FcPMe$_2$. Prepared from ferrocene (1.12 g, 6.03 mmol, 1.0 eq.), $AlCl_3$ (965 mg, 7.24 mmol, 1.2 eq.) and **1a** (2 M in toluene, 3.0 mL, 6.03 mmol, 1.0 eq.); 705 mg (2.87 mmol, 48%), red oil. The observed analytical results were in accordance with previously published data.[20]

Dibutylferrocenylphosphine (2b) FcPBu$_2$. Prepared from ferrocene (1.04 g, 5.60 mmol, 1.0 eq.), $AlCl_3$ (820 mg, 6.15 mmol, 1.1 eq.) and **1b** (1.21 g, 6.72 mmol, 1.2 eq.); 1.63 g (4.93 mmol, 88%), red oil. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = −35.9 ppm; ^1H NMR (300.1 MHz, $CDCl_3$): δ = 0.93 (t, $^3J_{HH}$ = 6.9 Hz, 6H, $P(CH_2)_3\mathit{Me}$), 1.39–1.46 (m, 8H, $P(CH_2)_2CH_2Me$, PCH_2CH_2Et), 1.59–1.64 (m, 4H, $PCH_2{}^nPr$), 4.18 (s, 5H, $H_{Cp'}$), 4.22 (q, $^{3/4}J_{HH}$ = 1.8 Hz, 2H, H_{Cp}), 4.30 (t, $^{3/4}J_{HH}$ = 1.8 Hz, 2H,

H_{Cp}) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 13.8 (s, $P(CH_2)_3$*Me*), 24.4 (d, $^1J_{CP}$ = 11.8 Hz, C-4a), 28.3 (d, $^{2/3}J_{CP}$ = 9.8 Hz, $P(CH_2)_2$*C*H_2Me/PCH_2*C*H_2Et), 28.5 (d, $^{2/3}J_{CP}$ = 14.4 Hz, $P(CH_2)_2$*C*H_2Me/PCH_2*C*H_2Et), 68.8 (s, $C_{Cp'}$), 69.7 (d, $^{2/3}J_{CP}$ = 3.4 Hz, C_{Cp}), 71.1 (d, $^{2/3}J_{CP}$ = 13.0 Hz, C_{Cp}), 79.0 (d, $^1J_{CP}$ = 12.2 Hz, $C_{Cp,ipso}$) ppm. MS (EI+) *m*/*z* = 330.1202 ($C_{18}H_{27}FeP$ requires 330.1200). IR (neat): ν = 3094 (w), 2954 (m), 2926 (s), 2870 (m), 2856 (m), 1463 (m), 1412 (m), 1377 (m), 1261 (w), 1193 (w), 1159 (m), 1106 (m), 1091 (m), 1024 (m), 1001 (m), 967 (m), 887 (m), 816 (s), 718 (m), 641 (w), 626 (w), 485 (s), 454 (m), 436 (m) cm^{-1}.

Dihexylferrocenylphosphine (2c) FcPHex$_2$. Prepared from ferrocene (939 mg, 5.05 mmol, 1.0 eq.), $AlCl_3$ (740 mg, 5.55 mmol, 1.1 eq.) and **1c** (1.43 g, 6.06 mmol, 1.2 eq.); 1.31 g (3.38 mmol, 67%), red oil. $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ = −35.5 ppm; ^1H NMR (300.1 MHz, C_6D_6): δ = 0.88 (t, $^3J_{HH}$ = 6.9 Hz, 6H, $P(CH_2)_5$*Me*), 1.19–1.31 (m, 8H, $P(CH_2)_4CH_2$Me, $P(CH_2)_3CH_2$Et), 1.34–1.45 (m, 4H, $PCH_2CH_2{}^n$Bu), 1.48–1.62 (m, 4H, $P(CH_2)_2CH_2{}^n$Pr), 1.63–1.72 (m, 4H, $PCH_2{}^n$Pent), 4.10 (s, 5H, $H_{Cp'}$), 4.10–4.11 (m, 2H, H_β), 4.19–4.21 (m, 2H, H_α) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ = 14.3 (s, $P(CH_2)_5$*Me*), 23.0 (s, $P(CH_2)_4CH_2$Me/$P(CH_2)_3CH_2$Et), 26.9 (d, $^3J_{CP}$ = 15.1 Hz, $P(CH_2)_2CH_2{}^n$Pr), 29.4 (d, $^1J_{CP}$ = 11.9 Hz, $PCH_2{}^n$Pent), 31.5 (d, $^2J_{CP}$ = 11.2 Hz, $PCH_2CH_2{}^n$Bu), 32.0 (s, $P(CH_2)_4CH_2$Me/$P(CH_2)_3CH_2$Et), 69.2 (s, $C_{Cp'}$), 70.1 (d, $^3J_{CP}$ = 3.1 Hz, C_β), 71.4 (d, $^2J_{CP}$ = 13.1 Hz, C_α), 80.1 (d, $^1J_{CP}$ = 15.5 Hz, $C_{Cp,ipso}$) ppm. MS (EI+) *m*/*z* = 386.1818 ($C_{22}H_{35}FeP$ requires 386.1826). IR (neat): ν = 3096 (w), 2954 (m), 2921 (s), 2853 (s), 1457 (m), 1412 (w), 1378 (w), 1192 (w), 1159 (m), 1106 (m), 1052 (m), 1025 (m), 1001 (m), 975 (m), 889 (w), 816 (s), 718 (m), 486 (s), 445 (m) cm^{-1}.

General procedure for the protonation of phosphines with bis(trifluoromethanesulfonyl)amine (3)

To a dichloromethane solution of the appropriate phosphine (1.1 eq.) bis(trifluoromethanesulfonyl)amine (1.0 eq.) was added and the resulting solution was stirred at ambient temperature for 2 h. The reaction mixture was evaporated to dryness and the crude product was washed several times with *n*-pentane. After drying in a vacuum the desired phosphonium compounds were obtained as viscous oils.

Dibutylferrocenylphosphonium bis(trifluoromethanesulfonyl)imide (3a). Prepared from **2b** (217 mg, 0.66 mmol, 1.1 eq.) and bis(trifluoromethanesulfonyl)amine (131 mg, 0.60 mmol, 1.0 eq.); 310 mg (0.51 mmol, 85%) orange oil. Anal. calc. for $C_{20}H_{28}F_6FeNO_4PS_2$ (611.39 g mol^{-1}) C 39.29, H 4.62, N 2.29%; found C 39.48, H 4.28, N 2.61%. ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ = 10.6 (dm, $^1J_{PH}$ = 496.1 Hz) ppm; ^1H NMR (300.1 MHz, CD_2Cl_2): δ = 0.98 (t, $^3J_{HH}$ = 7.2 Hz, 6H, $P(CH_2)_3$*Me*), 1.46–1.58 (m, 4H, $P(CH_2)_2CH_2$Me), 1.59–1.73 (m, 4H, PCH_2CH_2Et), 2.28–2.42 (m, 4H, $PCH_2{}^n$Pr), 4.41 (s, 5H, $H_{Cp'}$), 4.63 (quart, $^3J_{HH}$ = 1.9 Hz, 2H, H_α), 4.79 (quart, $^4J_{HH}$ = 1.8 Hz, 2H, H_β), 6.90 (dquint, $^1J_{PH}$ = 496.0 Hz, $^4J_{HH}$ = 5.3 Hz, 1H, P*H*) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ = 13.4 (s, $P(CH_2)_3$*Me*), 20.2 (d, $^1J_{CP}$ = 49.4 Hz, $PCH_2{}^n$Pr), 24.0 (d, $^3J_{CP}$ = 15.6 Hz, $P(CH_2)_2CH_2$Me), 25.1 (d, $^2J_{CP}$ = 4.4 Hz, PCH_2CH_2Et), 52.9 (d, overlain by CD_2Cl_2-signal, $C_{Cp,ipso}$), 71.1 (s, $C_{Cp'}$), 72.6 (d, $^2J_{CP}$ = 13.2 Hz, C_α), 74.9 (d, $^3J_{CP}$ = 10.6 Hz, C_β) ppm, CF_3-resonance has not been obtained; ^{19}F NMR (282.4 MHz, CD_2Cl_2): δ = −79.6 ppm. MS (APCI+, DCM) *m*/*z* (%) = 331.1271 (100, $[M - NTf_2]^+$ requires 331.1272); MS (APCI−, DCM) *m*/*z* (%) = 279.9178 (100, $[NTf_2]^-$ requires 279.9178). IR (neat): ν = 3108 (w), 2964 (m), 2936 (m), 2876 (m), 1466 (m), 1440 (m), 1416 (s), 1329 (s), 1225 (m), 1178 (vs), 1132 (s), 1051 (s), 935 (m), 875 (m), 829 (m), 788 (m), 762 (m), 738 (m), 653 (m), 599 (s), 569 (s), 508 (s), 462 (m) cm^{-1}.

Dibutylphenylphosphonium bis(trifluoromethanesulfonyl)imide (3b). Prepared from dibutylphenylphosphine (765 mg, 3.44 mmol, 1.1 eq.) and bis(trifluoromethanesulfonyl)amine (879 mg, 3.13 mmol, 1.0 eq.); 1.49 g (2.96 mmol, 95%) colorless oil. Anal. calc. for $C_{16}H_{24}F_6NO_4PS_2$ (503.46 g mol^{-1}) C 38.17, H 4.80, N 2.78%; found C 38.28, H 4.66, N 2.77%. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 14.2 (dm, $^1J_{PH}$ = 490.2 Hz) ppm; ^1H NMR (300.1 MHz, $CDCl_3$): δ = 0.87 (t, $^3J_{HH}$ = 7.1 Hz, 6H, $P(CH_2)_3$*Me*), 1.37–1.64 (m, 8H, $P(CH_2)_2CH_2$Me, PCH_2CH_2Et), 2.43–2.57 (m, 4H, $PCH_2{}^n$Pr), 6.90 (dquint, $^1J_{PH}$ = 489.7 Hz, $^4J_{HH}$ = 6.5 Hz, 1H, P*H*) 7.64–7.68 (m, 2H, $H_{o\text{-Ph}}$), 7.76–7.86 (m, 3H, $H_{m\text{-Ph}}$, $H_{p\text{-Ph}}$) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 13.0 (s, $P(CH_2)_3$*Me*), 19.1 (d, $^1J_{CP}$ = 46.6 Hz, $PCH_2{}^n$Pr), 23.2 (d, $^3J_{CP}$ = 15.7 Hz, $P(CH_2)_2CH_2$Me), 24.6 (d, $^2J_{CP}$ = 4.7 Hz, PCH_2CH_2Et), 114.4 (d, $^1J_{CP}$ = 82.5 Hz, $C_{Ph,ipso}$), 119.8 (q, $^1J_{CF}$ = 321.4 Hz, CF_3), 130.5 (d, $^2J_{CP}$ = 12.7 Hz, $C_{o\text{-Ph}}$), 132.8 (d, $^3J_{CP}$ = 10.2 Hz, $C_{m\text{-Ph}}$), 135.2 (d, $^4J_{CP}$ = 2.3 Hz, $C_{p\text{-Ph}}$) ppm; ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = −78.9 ppm. MS (ESI+, MeOH) *m*/*z* (%) = 223.1608 (100, $[M - NTf_2]^+$ requires 223.1610); MS (ESI−, MeOH) *m*/*z* (%) = 279.9179 (61, $[NTf_2]^-$ requires 279.9178). IR (neat): ν = 2965 (m), 2937 (m), 2877 (w), 1467 (w), 1442 (m), 1346 (s), 1328 (s), 1225 (m), 1178 (s), 1131 (s), 1051 (s), 999 (m), 965 (w), 937 (m), 876 (w), 788 (m), 739 (m), 722 (m), 691 (m), 653 (m), 612 (s), 599 (s), 569 (s), 480 (m), 452 (m) cm^{-1}.

Dibutylferrocenylphosphonium tetrachloroaluminate (3c). 100 mg ferrocene (0.54 mmol, 1.0 eq.) and 79 mg $AlCl_3$ (0.59 mmol, 1.1 eq.) were suspended in 15 mL *n*-heptane. 117 mg **1b** (0.65 mmol, 1.2 eq.) were added *via* a syringe and the reaction mixture was heated to reflux for 1.5 h whereupon a dark green oil was formed. The oil was washed with *n*-pentane several times until unreacted starting materials had been separated forming a deep orange solid. The solid was dried in a vacuum yielding 251 mg **3c** (0.50 mmol, 93%). ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ = 13.1 (dm, $^1J_{PH}$ = 489.4 Hz) ppm; ^1H NMR (300.1 MHz, CD_2Cl_2): δ = 0.87–1.10 (m, 6H, $P(CH_2)_3$*Me*), 1.41–1.64 (m, 4H, $P(CH_2)_2CH_2$Me), 1.65–1.87 (m, 4H, PCH_2CH_2Et), 2.28–2.56 (m, 4H, $PCH_2{}^n$Pr), 4.44 (s, 5H, $H_{Cp'}$), 4.46 (s, 2H, H_α), 4.83 (s, 2H, H_β), 6.90 (dm, $^1J_{PH}$ = 487.0 Hz, 1H, P*H*) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ = 13.6 (s, $P(CH_2)_3$*Me*), 20.9 (d, $^1J_{CP}$ = 48.0 Hz, $PCH_2{}^n$Pr), 24.2 (d, $^3J_{CP}$ = 15.5 Hz, $P(CH_2)_2CH_2$Me), 25.5 (d, $^2J_{CP}$ = 3.7 Hz, PCH_2CH_2Et), 52.8 (d, overlain by CD_2Cl_2-signal, $C_{Cp,ipso}$), 71.4 (s, $C_{Cp'}$), 73.1 (d, $^2J_{CP}$ = 13.3 Hz, C_α), 75.2 (d, $^3J_{CP}$ = 10.6 Hz, C_β) ppm;[27] Al NMR (104.2 MHz, CD_2Cl_2): δ = 103.8 ppm. MS (APCI+, DCM) *m*/*z* (%) = 331.1271 (100, $[M - AlCl_4]^+$ requires

331.1272); MS (APCI−, DCM) *m*/*z* (%) = 168.8546 (15, $[AlCl_4]^-$ requires 168.8545). IR (neat): ν = 3105 (w), 2961 (m), 2932 (m), 2873 (m), 1464 (m), 1414 (m), 1383 (m), 1347 (m), 1310 (w), 1187 (m), 1095 (m), 1036 (m), 1002 (m), 963 (m), 907 (m), 834 (m), 717 (m), 562 (m), 477 (vs) cm^{-1}.

General procedure for the preparation of trialkylferrocenyl-phosphonium halides (4)

The appropriate phosphine **2** (1.0 eq.) was dissolved in a sufficient amount of acetonitrile and the corresponding alkyl-halide (1.2 eq.) was added. The reaction mixture was heated to 60 °C for 12 h (in case of methyl iodide as an alkylation agent the reaction was carried out at ambient temperature). All volatile components were removed in a vacuum and the crude product was washed two times with 20 mL *n*-pentane. The desired trialkylferrocenyl-phosphonium halides **4** were dried in a vacuum (0.01 mbar) for one day.

Trimethylferrocenylphosphonium iodide (4a) [FcPMe$_3$]I. Prepared from **2a** (83 mg, 0.34 mmol, 1.0 eq.) and methyl iodide (72 mg, 0.51 mmol, 1.5 eq.); 113 mg (0.27 mmol, 85%) yellow solid. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3CN): δ = 25.0 ppm; ^1H NMR (300.1 MHz, CD_3CN): δ = 2.07 (d, $^2J_{HP}$ = 14.4 Hz, 9H, H-1a), 4.42 (s, 5H, $H_{Cp'}$), 4.67 (q, $^3J_{HH}$ = 1.8 Hz, 2H, H_{Cp}), 4.75 (q, $^3J_{HH}$ = 1.8 Hz, 2H, H_{Cp}) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_3CN): δ = 11.5 (d, $^1J_{CP}$ = 58.7 Hz, C-1a), 62.9 (d, $^1J_{CP}$ = 100.9 Hz, $C_{Cp,ipso}$), 71.0 (s, $C_{Cp'}$), 72.1 (d, $^{2/3}J_{CP}$ = 13.7 Hz, C_{Cp}), 74.5 (d, $^{2/3}J_{CP}$ = 10.6 Hz, C_{Cp}) ppm. MS (ESI+, MeOH) *m*/*z* (%) = 261.0486 (100, $[M - I]^+$ requires 261.0490). IR (neat): ν = 3054 (m), 2959 (m), 2895 (m), 2880 (m), 1409 (m), 1364 (w), 1304 (m), 1295 (m), 1188 (s), 1106 (m), 1073 (w), 1040 (s), 999 (m), 966 (vs), 953 (vs), 889 (m), 867 (m), 841 (vs), 807 (s), 784 (m), 770 (s), 688 (m), 613 (m), 506 (s), 484 (vs), 442 (vs) cm^{-1}. T_m: 276.9 °C (T_d: 299.7 °C). Single crystals suitable for XRD obtained from a saturated chloroform solution at ambient temperature.

Dimethylpropylferrocenylphosphonium bromide (4b) [FcPMe$_2$Pr]Br. Prepared from **2a** (189 mg, 0.77 mmol, 1.0 eq.) and 1-bromopropane (142 mg, 1.15 mmol, 1.5 eq.); 232 mg (0.63 mmol, 82%) orange solid. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 26.2 ppm; ^1H NMR (300.1 MHz, $CDCl_3$): δ = 1.00 (dt, $^3J_{HH}$ = 7.0 Hz, $^4J_{HP}$ = 1.1 Hz, 3H, H-1b), 1.42–1.58 (m, 2H, H-2b), 2.35 (d, $^2J_{HP}$ = 14.0 Hz, 6H, H-1a), 2.45–2.55 (m, 2H, H-3b), 4.33 (s, 5H, $H_{Cp'}$), 4.64–4.70 (m, 4H, H_{Cp}) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 9.9 (d, $^1J_{CP}$ = 57.6 Hz, C-1a), 15.2 (d, $^2J_{CP}$ = 16.9 Hz, C-2b), 15.9 (d, $^3J_{CP}$ = 4.2 Hz, C-1b), 27.8 (d, $^1J_{CP}$ = 52.5 Hz, C-3b), 61.2 (d, $^1J_{CP}$ = 96.6 Hz, $C_{Cp,ipso}$), 70.2 (s, $C_{Cp'}$), 71.5 (d, $^{2/3}J_{CP}$ = 12.9 Hz, C_{Cp}), 73.6 (d, $^{2/3}J_{CP}$ = 10.3 Hz, C_{Cp}) ppm. MS (ESI+, MeOH) *m*/*z* (%) = 289.0798 (100, $[M - Br]^+$ requires 289.0803). IR (neat): ν = 3048 (m), 2958 (m), 2874 (m), 1456 (m), 1411 (m), 1391 (m), 1367 (m), 1350 (w), 1311 (m), 1299 (m), 1244 (w), 1216 (w), 1187 (s), 1105 (m), 1083 (m), 1055 (s), 1037 (s), 1002 (m), 964 (m), 941 (vs), 884 (s), 782 (s), 723 (m), 656 (m), 617 (m), 484 (vs), 459 (s), 439 (s) cm^{-1}. T_m: 125.6 °C (T_d: 200.4 °C).

Dimethylbutylferrocenylphosphonium bromide (4c) [FcPMe$_2$Bu]Br. Prepared from **2a** (168 mg, 0.68 mmol, 1.0 eq.) and 1-bromobutane (140 mg, 1.02 mmol, 1.5 eq.); 218 mg (0.57 mmol, 84%) orange solid. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 26.5 ppm; ^1H NMR (300.1 MHz, $CDCl_3$): δ = 0.85 (t, $^3J_{HH}$ = 6.9 Hz, 3H, H-1b), 1.33–1.45 (m, 4H, H-2b, H-3b), 2.35 (d, $^2J_{HP}$ = 14.0 Hz, 6H, H-1a), 2.47–2.57 (m, 2H, H-4b), 4.33 (s, 5H, $H_{Cp'}$), 4.65 (s, 2H, H_{Cp}), 4.66 (s, 2H, H_{Cp}) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 9.9 (d, $^1J_{CP}$ = 57.6 Hz, C-1a), 13.5 (s, C-1b), 23.5 (d, $^2J_{CP}$ = 16.3 Hz, C-2b), 24.0 (d, $^3J_{CP}$ = 4.5 Hz, C-3b), 25.7 (d, $^1J_{CP}$ = 52.8 Hz, C-4b), 61.2 (d, $^1J_{CP}$ = 96.6 Hz, $C_{Cp,ipso}$), 70.2 (s, $C_{Cp'}$), 71.5 (d, $^{2/3}J_{CP}$ = 12.8 Hz, C_{Cp}), 73.6 (d, $^{2/3}J_{CP}$ = 10.3 Hz, C_{Cp}) ppm. MS (ESI+, MeOH) *m*/*z* (%) = 303.0955 (100, $[M - Br]^+$ requires 303.0960). IR (neat): ν = 3098 (w), 3053 (m), 2955 (m), 2931 (m), 2863 (m), 1464 (w), 1412 (m), 1390 (m), 1367 (w), 1314 (m), 1301 (m), 1231 (w), 1188 (s), 1106 (m), 1073 (m), 1035 (m), 1001 (m), 967 (s), 950 (s), 890 (vs), 877 (m), 846 (m), 823 (s), 777 (vs), 762 (m), 723 (m), 695 (m), 618 (w), 510 (m), 483 (vs), 443 (s), 427 (m) cm^{-1}. T_m: 155.0 °C (T_d: 217.2 °C).

Dibutylmethylferrocenylphosphonium iodide (4d) [FcPBu$_2$Me]I. Prepared from **2b** (156 mg, 0.47 mmol, 1.0 eq.) and methyl iodide (80 mg, 0.57 mmol, 1.2 eq.); 199 mg (0.58 mmol, 89%) orange highly viscous oil. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 29.4 ppm; ^1H NMR (300.1 MHz, $CDCl_3$): δ = 0.96 (t, $^3J_{HH}$ = 6.9 Hz, 6H, H-1a), 1.47–1.62 (m, 8H, H-2a, H-3a), 2.41 (d, $^2J_{HP}$ = 13.3 Hz, 3H, H-1b), 2.47–2.74 (m, 4H, H-4a), 4.39 (s, 5H, $H_{Cp'}$), 4.70 (quint, $^{3/4}J_{HH}$ = 1.8 Hz, 2H, H_{Cp}), 4.72 (quint, $^{3/4}J_{HH}$ = 1.8 Hz, 2H, H_{Cp}) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 8.6 (d, $^1J_{CP}$ = 56.4 Hz, C-1b), 13.6 (s, C-1a), 23.3 (d, $^1J_{CP}$ = 42.4 Hz, C-4a), 23.8 (d, $^{2/3}J_{CP}$ = 6.5 Hz, C-2a/C-3a), 24.1 (d, $^{2/3}J_{CP}$ = 4.5 Hz, C-2a/C-3a), 60.6 (d, $^1J_{CP}$ = 95.0 Hz, $C_{Cp,ipso}$), 70.3 (s, $C_{Cp'}$), 71.6 (d, $^{2/3}J_{CP}$ = 12.2 Hz, C_{Cp}), 73.6 (d, $^{2/3}J_{CP}$ = 10.1 Hz, C_{Cp}) ppm. MS (ESI+, MeOH) *m*/*z* (%) = 345.1423 (100, $[M - I]^+$ requires 345.1429). IR (neat): ν = 3052 (m), 2955 (s), 2929 (s), 2869 (s), 1461 (m), 1410 (m), 1391 (m), 1368 (m), 1308 (m), 1226 (m), 1185 (vs), 1105 (m), 1036 (s), 1002 (m), 969 (m), 931 (s), 883 (s), 823 (vs), 720 (m), 616 (w), 486 (vs), 465 (vs) cm^{-1}.

Dibutylpropylferrocenylphosphonium bromide (4e) [FcPBu$_2$Pr]Br. Prepared from **2b** (173 mg, 0.52 mmol, 1.0 eq.) and 1-bromopropane (77 mg, 0.63 mmol, 1.2 eq.); 203 mg (0.45 mmol, 87%) orange solid. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 30.7 ppm; ^1H NMR (300.1 MHz, $CDCl_3$): δ = 0.97 (t, $^3J_{HH}$ = 7.1 Hz, 6H, H-1a), 1.17 (dt, $^3J_{HH}$ = 7.1 Hz, $^4J_{HP}$ = 1.5 Hz, 3H, H-1b), 1.51–1.63 (m, 8H, H-2a, H-3a), 1.65–1.76 (m, 2H, H-2b), 2.60–2.72 (m, 6H, H-4a, H-3b), 4.37 (s, 5H, $H_{Cp'}$), 4.71 (s, 2H, H_{Cp}), 4.71 (s, 2H, H_{Cp}) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 13.6 (s, C-1a), 15.6 (d, $^3J_{CP}$ = 16.6 Hz, C-1b), 16.2 (d, $^2J_{CP}$ = 4.3 Hz, C-2b), 21.8 (d, $^1J_{CP}$ = 50.4 Hz, C-4a), 23.9 (d, $^2J_{CP}$ = 15.7 Hz, C-3a), 24.0 (d, $^1J_{CP}$ = 50.7 Hz, C-3b), 24.3 (d, $^3J_{CP}$ = 4.8 Hz, C-2a), 60.1 (d, $^1J_{CP}$ = 91.9 Hz, $C_{Cp,ipso}$), 70.3 (s, $C_{Cp'}$), 71.9 (d, $^{2/3}J_{CP}$ = 11.3 Hz, C_{Cp}), 73.5 (d, $^{2/3}J_{CP}$ = 9.7 Hz, C_{Cp}) ppm. MS (ESI+, MeOH) *m*/*z* (%) = 373.1735 (100, $[M - Br]^+$ requires 373.1742). IR (neat): ν = 3055 (m), 2956 (s), 2929 (s), 2868 (s), 2797 (m), 1460 (m), 1411 (m), 1393 (w), 1372 (m), 1351 (w), 1311 (w), 1234 (m), 1184 (s), 1106 (s), 1088 (m), 1067 (m), 1045 (m), 1001 (m), 971 (w), 896 (m), 846 (m), 819 (vs),

733 (s), 619 (w), 520 (w), 483 (vs), 464 (vs) cm^{-1}. T_m: 106.7 °C (T_d: 313.6 °C).

Tributylferrocenylphosphonium bromide (4f) [FcPBu$_3$]Br. Prepared from **2b** (177 mg, 0.54 mmol, 1.0 eq.) and 1-bromobutane (88 mg, 0.64 mmol, 1.2 eq.); 193 mg (0.41 mmol, 76%) orange solid. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 31.6 ppm; ^1H NMR (300.1 MHz, $CDCl_3$): δ = 0.93 (t, $^3J_{HH}$ = 6.9 Hz, 9H, H-1a), 1.48–1.61 (m, 12H, H-2a, H-3a), 2.58–2.68 (m, 6H, H-4a), 4.31 (s, 5H, $H_{Cp'}$), 4.66 (s, 2H, H_{Cp}), 4.67 (s, 2H, H_{Cp}) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 13.7 (s, C-1a), 22.0 (d, $^1J_{CP}$ = 50.5 Hz, C-4a), 24.0 (d, $^2J_{CP}$ = 15.7 Hz, C-3a), 24.4 (d, $^3J_{CP}$ = 4.7 Hz, C-2a), 60.2 (d, $^1J_{CP}$ = 91.9 Hz, $C_{Cp,ipso}$), 70.4 (s, $C_{Cp'}$), 72.0 (d, $^{2/3}J_{CP}$ = 11.1 Hz, C_{Cp}), 73.5 (d, $^{2/3}J_{CP}$ = 9.5 Hz, C_{Cp}), ppm. ESI-HRMS (MeOH): pos.: *m*/*z* (%) = $[M - Br]^+$ ber. 387.1899, gef. 387.1892 (100). IR (neat): ν = 3053 (w), 2955 (s), 2929 (s), 2868 (s), 2797 (m), 1460 (m), 1411 (m), 1393 (m), 1377 (m), 1351 (m), 1311 (m), 1227 (m), 1184 (w), 1106 (m), 1094 (m), 1066 (m), 1044 (m), 1001 (m), 971 (m), 897 (m), 845 (s), 818 (vs), 783 (s), 618 (w), 482 (s), 466 (vs) cm^{-1}. T_m: 129.3 °C (T_d: 339.6 °C).

General procedure for the preparation of ferrocenylphosphonium bis(trifluoromethanesulfonyl)imides (5)

Method A: The appropriate trisalkylferrocenylphosphonium halide **4** (1.0 eq.) was suspended in a 1 : 1 mixture of methanol–water and lithium bis(trifluoromethanesulfonyl)imide (1.1 eq.) was added. The resulting yellow suspension was stirred vigorously at 40 °C for 12 h. Under inert conditions the reaction mixture was extracted four times with 20 mL dichloromethane until the organic phase stayed colorless. The volume of the combined organic phases was reduced to 30 mL and washed three times with 20 mL ultrapure water (σ = 0.054 μS). The organic phase was evaporated to dryness and washed two times with 20 mL Et_2O and three times with 20 mL *n*-pentane. The desired product was dried under high vacuum (5×10^{-5}–7×10^{-6} mbar). *Method B*: The appropriate phosphine **2** (1.0 eq.) was dissolved in a sufficient amount of acetonitrile and $MeNTf_2$ (1.1 eq. and 2.0 eq. for **2e**) was added. The reaction mixture was stirred for 12 h at ambient temperature (in case of **2d** and **2e** the reaction was carried out at 60 °C for 12 h and 3 d, respectively). All volatile components were removed in a vacuum and the crude product was washed two times with 20 mL *n*-pentane. The desired product was dried in a vacuum (0.01 mbar) at 40 °C for one day. *Method C*: The appropriate heteroleptic sandwich complex [(η^5-C_5H_5)-Fe(η^6-arene)]NTf_2 (1.0 eq.) and the cyclopentadienylidene phosphorane (1.0 eq.) were dissolved in a sufficient amount of acetonitrile. The solution was irradiated with visible light (Osram Ultra Vitalux 300W) for 12 h. On subsequent removing the solvent in a vacuum the crude product was washed two times with Et_2O and two times with *n*-pentane to obtain the desired product after drying in a vacuum (0.01 mbar) for one day.

Trimethylferrocenylphosphonium bis(trifluoromethanesulfonyl)imide (5a) [FcPMe$_3$]NTf$_2$. 5a was prepared according to method A. **4a** (113 mg, 0.27 mmol, 1.0 eq.) and lithium bis(trifluoromethanesulfonyl)imide (98 mg, 0.34 mmol, 1.2 eq.); 114 mg (0.20 mmol, 74%) orange oil. Anal. calc. for $C_{15}H_{18}F_6FeNO_4PS_2$ (541.25 g mol^{-1}) C 33.29, H 3.35, N 2.59%; found C 33.63, H 3.15, N 2.58%. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3CN): δ = 25.0 ppm; ^1H NMR (300.1 MHz, CD_3CN): δ = 2.00 (d, $^2J_{HP}$ = 14.4 Hz, 9H, H-1a), 4.41 (s, 5H, $H_{Cp'}$), 4.63 (q, $^3J_{HH}$ = 1.9 Hz, 2H, H_{Cp}), 4.75 (q, $^3J_{HH}$ = 1.9 Hz, 2H, H_{Cp}) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_3CN): δ = 11.3 (d, $^1J_{CP}$ = 58.7 Hz, C-1a), 62.1 ($C_{Cp,ipso}$),[65] 71.1 (s, $C_{Cp'}$), 72.0 (d, $^{2/3}J_{CP}$ = 13.8 Hz, C_{Cp}), 74.7 (d, $^{2/3}J_{CP}$ = 10.7 Hz, C_{Cp}) ppm; ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = 79.5 ppm. MS (ESI+, MeOH) *m*/*z* (%) = 261.0487 (100, $[M - NTf_2]^+$ requires 261.0490); MS (ESI−, MeOH) *m*/*z* (%) = 279.9177 (100, $[NTf_2]^-$ requires 279.9178). IR (neat): ν = 3111 (w), 3004 (w), 2925 (w), 1421 (m), 1346 (s), 1330 (s), 1304 (m), 1225 (m), 1175 (vs), 1132 (vs), 1108 (m), 1050 (vs), 1004 (m), 958 (s), 889 (m), 870 (m), 831 (m), 787 (m), 763 (m), 739 (m), 685 (m), 653 (m), 612 (s), 599 (s), 568 (vs), 506 (vs), 484 (s), 436 (s) cm^{-1}. $E_{1/2}$ ([EMIM]NTf_2) = 458 mV *vs.* Fc/Fc^+.

Dimethylpropylferrocenylphosphonium bis(trifluoromethanesulfonyl)imide (5b) [FcPMe$_2$Pr]NTf$_2$. 5b was prepared according to method A. **4b** (232 mg, 0.63 mmol, 1.0 eq.) and lithium bis(trifluoromethanesulfonyl)imide (217 mg, 0.76 mmol, 1.2 eq.); 347 mg (0.61 mmol, 97%) orange oil. Anal. calc. for $C_{17}H_{22}F_6FeNO_4PS_2$ (569.30 g mol^{-1}) C 35.87, H 3.90, N 2.46%; found C 35.58, H 3.96, N 2.65%. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 26.9 ppm; ^1H NMR (300.1 MHz, $CDCl_3$): δ = 1.04 (dt, $^3J_{HH}$ = 7.3 Hz, $^4J_{HP}$ = 1.3 Hz, 3H, H-1b), 1.46–1.58 (m, 2H, H-2b), 2.09 (d, $^2J_{HP}$ = 13.7 Hz, 6H, H-1a), 2.15–2.23 (m, 2H, H-3b), 4.37 (s, 5H, $H_{Cp'}$), 4.57 (q, $^3J_{HH}$ = 1.9 Hz, 2H, H_{Cp}), 4.73 (q, $^3J_{HH}$ = 1.8 Hz, 2H, H_{Cp}) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 8.5 (d, $^1J_{CP}$ = 58.2 Hz, C-1a), 14.9 (d, $^2J_{CP}$ = 17.0 Hz, C-2b), 15.7 (d, $^3J_{CP}$ = 4.1 Hz, C-1b), 27.4 (d, $^1J_{CP}$ = 52.6 Hz, C-3b), 60.3 (d, $^1J_{CP}$ = 98.4 Hz, $C_{Cp,ipso}$), 70.3 (s, $C_{Cp'}$), 71.0 (d, $^{2/3}J_{CP}$ = 13.2 Hz, C_{Cp}), 74.0 (d, $^{2/3}J_{CP}$ = 10.5 Hz, C_{Cp}), 120.0 (q, $^1J_{CF}$ = 321.4 Hz, CF_3) ppm; ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = −78.8 ppm. MS (ESI+, MeOH) *m*/*z* (%) = 289.0799 (100, $[M - NTf_2]^+$ requires 289.0803); MS (ESI−, MeOH) *m*/*z* (%) = 279.9177 (100, $[NTf_2]^-$ requires 279.9178). IR (neat): ν = 3109 (w), 2972 (m), 2928 (m), 2881 (w), 1463 (w), 1416 (m), 1346 (s), 1330 (s), 1225 (m), 1176 (vs), 1133 (vs), 1108 (m), 1050 (vs), 1004 (m), 956 (s), 936 (m), 886 (m), 830 (m), 787 (m), 762 (m), 739 (m), 653 (m), 612 (s), 599 (s), 568 (s), 508 (s), 485 (s), 458 (m), 444 (s) cm^{-1}. $E_{1/2}$ ([EMIM]-NTf_2) = 458 mV *vs.* Fc/Fc^+.

Dimethylbutylferrocenylphosphonium bis(trifluoromethanesulfonyl)imide (5c) [FcPMe$_2$Bu]NTf$_2$. 5c was prepared according to method A. **4c** (218 mg, 0.57 mmol, 1.0 eq.) and lithium bis(trifluoromethanesulfonyl)imide (196 mg, 0.68 mmol, 1.2 eq.); 247 mg (0.42 mmol, 74%) orange oil. Anal. calc. for $C_{18}H_{24}F_6FeNO_4PS_2$ (583.34 g mol^{-1}) C 37.06, H 4.15, N 2.40%; found C 37.36, H 4.18, N 2.60%. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 27.3 ppm; ^1H NMR (300.1 MHz, $CDCl_3$): δ = 0.85 (t, $^3J_{HH}$ = 6.8 Hz, 3H, H-1b), 1.33–1.45 (m, 4H, H-2b, H-3b), 2.35 (d, $^2J_{HP}$ = 14.0 Hz, 6H, H-1a), 2.47–2.57 (m, 2H, H-4b), 4.33 (s, 5H, $H_{Cp'}$), 4.65 (s, 2H, H_{Cp}), 4.66 (s, 2H, H_{Cp}) ppm; $^{13}C\{^1H\}$

NMR (75.5 MHz, $CDCl_3$): δ = 8.5 (d, $^1J_{CP}$ = 58.2 Hz, C-1a), 13.2 (s, C-1b), 23.4 (d, $^2J_{CP}$ = 16.2 Hz, C-2b), 23.7 (d, $^3J_{CP}$ = 4.5 Hz, C-3b), 25.4 (d, $^1J_{CP}$ = 53.0 Hz, C-4b), 60.3 (d, $^1J_{CP}$ = 98.5 Hz, $C_{Cp,ipso}$), 70.3 (s, $C_{Cp'}$), 71.1 (d, $^{2/3}J_{CP}$ = 13.1 Hz, C_{Cp}), 74.0 (d, $^{2/3}J_{CP}$ = 10.5 Hz, C_{Cp}), 120.0 (q, $^1J_{CF}$ = 321.4 Hz, CF_3) ppm; ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = −78.8 ppm. MS (ESI+, MeOH) m/z (%) = 303.0956 (100, $[M - NTf_2]^+$ requires 303.0960); MS (ESI−, MeOH) m/z (%) = 279.9176 (100, $[NTf_2]^-$ requires 279.9178). IR (neat): ν = 3109 (w), 2964 (w), 2932 (m), 2877 (w), 1467 (w), 1416 (w), 1346 (s), 1330 (s), 1225 (m), 1176 (vs), 1133 (vs), 1108 (m), 1051 (vs), 1004 (m), 944 (s), 886 (m), 869 (m), 830 (s), 787 (s), 761 (m), 739 (m), 653 (m), 612 (s), 599 (s), 569 (s), 508 (s), 485 (s), 459 (m), 444 (m) cm^{-1}. $E_{1/2}$ ([EMIM]NTf_2) = 463 mV *vs.* Fc/Fc^+.

Dibutylmethylferrocenylphosphonium bis(trifluoromethanesulfonyl)imide (5d) [FcPBu$_2$Me]NTf$_2$. 5d was prepared according to method A. **4d** (199 mg, 0.58 mmol, 1.0 eq.) and lithium bis(trifluoromethanesulfonyl)imide (167 mg, 0.58 mmol, 1.0 eq.); 264 mg (0.42 mmol, 72%) orange oil. Anal. calc. for $C_{21}H_{30}F_6FeNO_4PS_2$ (625.42 g mol^{-1}) C 40.33, H 4.83, N 2.24%; found C 40.68, H 5.01, N 2.55%. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 30.0 ppm; ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 0.95 (t, $^3J_{HH}$ = 6.8 Hz, 6H, H-1a), 1.43–1.55 (m, 8H, H-2a, H-3a), 2.07 (d, $^2J_{HP}$ = 13.2 Hz, 3H, H-1b), 2.20–2.32 (m, 4H, H-4a), 4.37 (s, 5H, $H_{Cp'}$), 4.56 (q, $^{3/4}J_{HH}$ = 1.8 Hz, 2H, H_{Cp}), 4.74 (q, $^{3/4}J_{HH}$ = 1.8 Hz, 2H, H_{Cp}) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 6.6 (d, $^1J_{CP}$ = 57.3 Hz, C-1b), 13.3 (s, C-1a), 22.9 (d, $^1J_{CP}$ = 52.2 Hz, C-4a), 23.6 (d, $^3J_{CP}$ = 15.9 Hz, C-2a), 23.8 (d, $^2J_{CP}$ = 4.5 Hz, C-3a), 59.8 (d, $^1J_{CP}$ = 96.1 Hz, $C_{Cp,ipso}$), 70.3 (s, $C_{Cp'}$), 71.2 (d, $^{2/3}J_{CP}$ = 12.3 Hz, C_{Cp}), 73.9 (d, $^{2/3}J_{CP}$ = 10.2 Hz, C_{Cp}), 120.0 (q, $^1J_{CF}$ = 321.5 Hz, CF_3) ppm; ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = −78.8 ppm. MS (ESI+, MeOH) m/z (%) = 345.1425 (100, $[M - NTf_2]^+$ requires 345.1429); MS (ESI−, MeOH) m/z (%) = 279.9177 (100, $[NTf_2]^-$ requires 279.9178). IR (neat): ν = 3109 (w), 2964 (m), 2936 (m), 2876 (m), 1720 (vw), 1466 (w), 1415 (w), 1347 (s), 1330 (s), 1225 (s), 1176 (vs), 1134 (vs), 1108 (m), 1051 (vs), 1004 (m), 969 (w), 928 (m), 882 (m), 830 (m), 787 (m), 761 (m), 739 (m), 652 (m), 613 (s), 599 (s), 569 (s), 509 (s), 486 (s), 463 (s) cm^{-1}. $E_{1/2}$ ([EMIM]NTf_2) = 454 mV *vs.* Fc/Fc^+.

Dibutylpropylferrocenylphosphonium bis(trifluoromethanesulfonyl)imide (5e) [FcPBu$_2$Pr]NTf$_2$. 5e was prepared according to method A. **4f** (203 mg, 0.45 mmol, 1.0 eq.) and lithium bis(trifluoromethanesulfonyl)imide (129 mg, 0.45 mmol, 1.0 eq.); 240 mg (0.37 mmol, 82%) orange oil. Anal. calc. for $C_{23}H_{34}F_6FeNO_4PS_2$ (653.47 g mol^{-1}) C 42.27, H 5.24, N 2.14%; found C 42.48, H 5.35, N 2.35%. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 31.8 ppm; ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 0.97 (t, $^3J_{HH}$ = 6.9 Hz, 6H, H-1a), 1.15 (dt, $^3J_{HH}$ = 7.2 Hz, $^4J_{HP}$ = 1.5 Hz, 3H, H-1b), 1.46–1.57 (m, 8H, H-2a, H-3a), 1.60–1.72 (m, 2H, H-2b), 2.22–2.32 (m, 6H, H-4a, H-3b), 4.36 (s, 5H, $H_{Cp'}$), 4.53 (q, $^3J_{HH}$ = 1.89 Hz, 2H, H_{Cp}), 4.75 (q, $^3J_{HH}$ = 1.9 Hz, 2H, H_{Cp}) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 13.3 (s, C-1a), 15.3 (d, $^3J_{CP}$ = 16.7 Hz, C-1b), 15.9 (d, $^2J_{CP}$ = 4.4 Hz, C-2b), 21.3 (d, $^1J_{CP}$ = 51.0 Hz, C-4a), 23.5 (d, $^1J_{CP}$ = 50.7 Hz, C-3b), 23.7 (d, $^2J_{CP}$ = 15.7 Hz, C-3a), 24.0 (d, $^3J_{CP}$ = 4.5 Hz, C-2a), 59.2 (d, $^1J_{CP}$ = 93.2 Hz, $C_{Cp,ipso}$), 70.4 (s, $C_{Cp'}$), 71.3 (d, $^{2/3}J_{CP}$ = 11.5 Hz, C_{Cp}), 73.8 (d, $^{2/3}J_{CP}$ = 9.8 Hz, C_{Cp}), 120.0 (q, $^1J_{CF}$ = 321.5 Hz, CF_3) ppm; ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = −78.8 ppm. MS (ESI+, MeOH) m/z (%) = 373.1737 (100, $[M - NTf_2]^+$ requires 373.1743); MS (ESI−, MeOH) m/z (%) = 279.9177 (100, $[NTf_2]^-$ requires 279.9178). IR (neat): ν = 3110 (w), 2965 (m), 2937 (m), 2877 (m), 1465 (w), 1414 (w), 1383 (w), 1346 (s), 1330 (s), 1225 (m), 1176 (vs), 1134 (s), 1108 (m), 1098 (m), 1051 (s), 1004 (m), 911 (w), 830 (m), 787 (m), 761 (m), 738 (m), 652 (m), 613 (s), 599 (s), 568 (s), 509 (s), 486 (s), 465 (s) cm^{-1}. $E_{1/2}$ ([EMIM]NTf_2) = 453 mV *vs.* Fc/Fc^+.

Tributylferrocenylphosphonium bis(trifluoromethanesulfonyl)imide (5f) [FcPBu$_3$]NTf$_2$. 5f was prepared according to method A and C. *Method A*: **4f** (193 mg, 0.41 mmol, 1.0 eq.) and lithium bis(trifluoromethanesulfonyl)imide (119 mg, 0.41 mmol, 1.0 eq.); 244 mg (0.37 mmol, 89%) orange solid. *Method C*: **8b** (222 mg, 0.83 mmol, 1.2 eq.) and [(C_5H_5)Fe(η^6-toluene)]NTf_2 (343 mg, 0.70 mmol, 1.0 eq.); 444 mg (0.67 mmol, 95%) orange solid. Anal. calc. for $C_{24}H_{36}F_6FeNO_4PS_2$ (667.50 g mol^{-1}) C 43.19, H 5.44, N 2.10%; found C 43.47, H 5.55, N 2.45%. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 32.1 ppm; ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 0.97 (t, $^3J_{HH}$ = 6.8 Hz, 9H, H-1a), 1.47–1.62 (m, 12H, H-2a, H-3a), 2.24–2.33 (m, 6H, H-4a), 4.36 (s, 5H, $H_{Cp'}$), 4.54 (d, $^3J_{HH}$ = 1.6 Hz, 2H, H_{Cp}), 4.76 (d, $^3J_{HH}$ = 1.6 Hz, 2H, H_{Cp}) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 13.3 (s, C-1a), 21.3 (d, $^1J_{CP}$ = 51.0 Hz, C-4a), 23.7 (d, $^2J_{CP}$ = 15.7 Hz, C-3a), 24.0 (d, $^3J_{CP}$ = 4.6 Hz, C-2a), 59.3 (d, $^1J_{CP}$ = 93.3 Hz, $C_{Cp,ipso}$), 70.4 (s, $C_{Cp'}$), 71.3 (d, $^{2/3}J_{CP}$ = 11.5 Hz, C_{Cp}), 73.8 (d, $^{2/3}J_{CP}$ = 9.8 Hz, C_{Cp}), 120.0 (q, $^1J_{CF}$ = 321.9 Hz, CF_3) ppm; ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = −78.8 ppm. MS (ESI+, MeOH) m/z (%) = 387.1894 (100, $[M - NTf_2]^+$ requires 387.1899); MS (ESI−, MeOH) m/z (%) = 279.9177 (100, $[NTf_2]^-$ requires 279.9178). IR (neat): ν = 3114 (w), 2966 (m), 2937 (m), 2877 (w), 1466 (w), 1409 (w), 1383 (w), 1348 (s), 1336 (s), 1222 (m), 1180 (vs), 1138 (s), 1107 (m), 1099 (m), 1051 (s), 1036 (s), 1003 (m), 968 (w), 907 (m), 894 (w), 850 (m), 824 (s), 789 (m), 761 (w), 738 (m), 724 (m), 613 (s), 568 (s), 512 (s), 486 (s), 467 (s), 407 (m) cm^{-1}. T_m: 72.4 °C (T_d: 327.4 °C). Single crystals suitable for XRD obtained by slow diffusion of Et_2O into an acetonitrile solution. $E_{1/2}$ ([EMIM]NTf_2) = 454 mV *vs.* Fc/Fc^+.

Dihexylmethylferrocenylphosphonium bis(trifluoromethanesulfonyl)imide (5g) [FcPHex$_2$Me]NTf$_2$. 5g was prepared according to method B. **2c** (570 mg, 1.48 mmol, 1.0 eq.) and $MeNTf_2$ (479 mg, 1.62 mmol, 1.1 eq.); 860 mg (1.26 mmol, 85%) red oil. Anal. calc. for $C_{25}H_{38}F_6FeNO_4PS_2$ (681.51 g mol^{-1}) C 44.06, H 5.62, N 2.06%; found C 44.39, H 5.69, N 2.30%. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 29.9 ppm; ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 0.88 (t, $^3J_{HH}$ = 6.9 Hz, 9H, H-1a), 1.23–1.35 (m, 8H, H-2a, H-3a), 1.40–1.60 (m, 8H, H-4a, H-5a), 2.07 (d, $^2J_{PH}$ = 13.2 Hz, 3H, H-1b), 2.16–2.34 (m, 4H, H-6a), 4.37 (s, 5H, $H_{Cp'}$), 4.55 (q, $^3J_{HH}$ = 1.8 Hz, 2H, H_{Cp}), 4.74 (q, $^3J_{HH}$ = 1.8 Hz, 2H, H_{Cp}) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 6.6 (d, $^1J_{CP}$ = 57.3 Hz, C-1b), 13.8 (s, C-1a), 21.8 (d, $^2J_{CP}$ = 4.3 Hz, C-5a), 22.3 (s, C-2a), 23.1 (d, $^1J_{CP}$ = 51.9 Hz, C-6a), 30.1 (d, $^3J_{CP}$ = 15.4 Hz, C-4a), 30.9 (s, C-3a), 59.8 (d, $^1J_{CP}$ = 95.9 Hz, $C_{Cp,ipso}$),

70.3 (s, $C_{Cp'}$), 71.1 (d, $^{2/3}J_{CP}$ = 12.2 Hz, C_{Cp}), 73.9 (d, $^{2/3}J_{CP}$ = 10.1 Hz, C_{Cp}), ppm, CF_3-resonance has not been obtained; ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = −78.7 ppm. MS (ESI+, MeOH) *m*/*z* (%) = 401.2052 (100, $[M - NTf_2]^+$ requires 401.2054); MS (ESI−, MeOH) *m*/*z* (%) = 279.9177 (100, $[NTf_2]^-$ requires 279.9178). IR (neat): ν = 3108 (w), 2957 (m), 2931 (m), 2862 (m), 1466 (w), 1415 (w), 1347 (s), 1331 (s), 1225 (m), 1177 (vs), 1134 (s), 1108 (m), 1052 (s), 1004 (m), 912 (m), 882 (m), 830 (m), 787 (m), 761 (m), 738 (m), 652 (m), 614 (s), 599 (s), 569 (s), 510 (s), 485 (m), 407 (w). $E_{1/2}$ ([EMIM]NTf_2) = 453 mV *vs.* Fc/Fc^+.

Diphenylmethylferrocenylphosphonium bis(trifluoromethanesulfonyl)imide (5h) [FcPPh$_2$Me]NTf$_2$. 5h was prepared according to method B. **2d** (507 mg, 1.37 mmol, 1.0 eq.) and $MeNTf_2$ (485 mg, 1.64 mmol, 1.2 eq.); 875 mg (1.32 mmol, 96%) red oil. Anal. calc. for $C_{25}H_{22}F_6FeNO_4PS_2$ (664.39 g mol^{-1}) C 45.13, H 3.33, N 2.11%; found C 45.46, H 3.34, N 2.37%. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3CN): δ = 22.6 ppm; ^{1}H NMR (300.1 MHz, CD_3CN): δ = 2.73 (d, $^2J_{PH}$ = 13.8 Hz, 3H, H-1b), 4.25 (s, 5H, $H_{Cp'}$), 4.59 (q, $^3J_{HH}$ = 1.9 Hz, 2H, H_{Cp}), 4.89 (q, $^3J_{HH}$ = 1.9 Hz, 2H, H_{Cp}), 7.64–7.72 (m, 8H, $H_{o\text{-}Ph}$, $H_{m\text{-}Ph}$), 7.79–7.86 (m, 2H, $H_{p\text{-}Ph}$) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_3CN): δ = 9.5 (d, $^1J_{CP}$ = 61.6 Hz, C-1b), 61.1 (d, $^1J_{CP}$ = 105.0 Hz, $C_{Cp,ipso}$), 71.5 (s, $C_{Cp'}$), 73.6 (d, $^{2/3}J_{CP}$ = 13.2 Hz, C_{Cp}), 75.7 (d, $^{2/3}J_{CP}$ = 10.8 Hz, C_{Cp}), 120.9 (q, $^1J_{CF}$ = 320.9 Hz, CF_3), 122.7 (d, $^1J_{CP}$ = 90.7 Hz, $C_{Ph,ipso}$), 130.8 (d, $^2J_{CP}$ = 12.8 Hz, $C_{o\text{-}Ph}$), 133.4 (d, $^3J_{CP}$ = 10.8 Hz, $C_{m\text{-}Ph}$), 135.6 (d, $^4J_{CP}$ = 3.0 Hz, $C_{p\text{-}Ph}$) ppm; ^{19}F NMR (282.4 MHz, CD_3CN): δ = −79.4 ppm. MS (ESI+, MeOH) *m*/*z* (%) = 385.0794 (100, $[M - NTf_2]^+$ requires 385.0803); MS (ESI−, MeOH) *m*/*z* (%) = 279.9178 (61, $[NTf_2]^-$ requires 279.9178). IR (neat): ν = 3103 (w), 3064 (w), 3000 (w), 2925 (w), 1439 (m), 1416 (w), 1348 (s), 1330 (s), 1176 (vs), 1133 (vs), 1110 (s), 1050 (vs), 998 (m), 895 (m), 881 (m), 833 (m), 785 (m), 740 (s), 718 (m), 689 (s), 652 (m), 609 (s), 568 (s), 538 (s), 510 (m), 465 (s), 443 (m). $E_{1/2}$ ([EMIM]NTf_2) = 504 mV *vs.* Fc/Fc^+.

Triphenylferrocenylphosphonium bis(trifluoromethanesulfonyl)imide (5i) [FcPPh$_3$]NTf$_2$. 5i was prepared according to method C. **8a** (230 mg, 0.70 mmol, 1.0 eq.) and $[(C_5H_5)Fe(\eta^6\text{-toluene})]NTf_2$ (379 mg, 0.70 mmol, 1.0 eq.); 490 mg (0.67 mmol, 96%) yellow solid. Anal. calc. for $C_{30}H_{24}F_6FeNO_4PS_2$ (727.46 g mol^{-1}) C 49.53, H 3.33, N 1.93%; found C 49.31, H 3.33, N 2.16%. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 28.1 ppm; ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 4.15 (s, 5H, $H_{Cp'}$), 4.51 (s, 2H, H_{Cp}), 4.91 (s, 2H, H_{Cp}), 7.51–7.95 (m, 10H, $H_{o\text{-}Ph}$, $H_{m\text{-}Ph}$, $H_{p\text{-}Ph}$) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 59.7 (d, $^1J_{CP}$ = 105.0 Hz, $C_{Cp,ipso}$), 71.0 (s, $C_{Cp'}$), 74.2 (d, $^{2/3}J_{CP}$ = 13.1 Hz, C_{Cp}), 75.0 (d, $^{2/3}J_{CP}$ = 10.9 Hz, C_{Cp}), 120.0 (d, $^1J_{CP}$ = 91.9 Hz, $C_{Ph,ipso}$), 130.4 (d, $^2J_{CP}$ = 12.9 Hz, $C_{o\text{-}Ph}$), 133.5 (d, $^3J_{CP}$ = 10.5 Hz, $C_{m\text{-}Ph}$), 135.4 (d, $^4J_{CP}$ = 2.7 Hz, $C_{p\text{-}Ph}$) ppm, CF_3-resonance has not been obtained; ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = −77.8 ppm. MS (ESI+, MeOH) *m*/*z* (%) = 447.0964 (100, $[M - (NTf_2)]^+$ requires 447.0960); MS (ESI−, MeOH) *m*/*z* (%) = 279.9179 (13, $[NTf_2]^-$ requires 279.9178). IR (neat): ν = 3106 (w), 3065 (w), 1588 (w), 1485 (w), 1439 (m), 1414 (w), 1394 (w), 1348 (s), 1331 (s), 1221 (m), 1194 (s), 1175 (vs), 1134 (s), 1111 (s), 1048 (vs), 1034 (s), 998 (m), 911 (w), 841 (m), 830 (m), 789 (m), 759 (m), 749 (m), 739 (m), 726 (s), 693 (s), 613 (w), 563 (s), 532 (s), 513 (s), 492 (s), 460 (m), 447 (m). $E_{1/2}$ ([EMIM]NTf_2) = 523 mV *vs.* Fc/Fc^+.

1,1′-Bis(diphenylmethyl)ferrocendiylphosphonium bis(trifluoromethanesulfonyl)imide (5j) [Fc(PPh$_2$Me)$_2$][NTf$_2$]$_2$. 5j was prepared according to method B. dppf (400 mg, 0.72 mmol, 1.0 eq.) and $MeNTf_2$ (425 mg, 1.44 mmol, 2.0 eq.); 643 mg (0.56 mmol, 78%) pale brown solid. Anal. calc. for $C_{40}H_{34}F_{12}FeN_2O_8P_2S_4$ (1144.74 g mol^{-1}) C 41.97, H 2.99, N 2.45%; found C 42.02, H 3.07, N 2.60%. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3CN): δ = 21.9 ppm; ^{1}H NMR (300.1 MHz, CD_3CN): δ = 2.59 (d, $^2J_{PH}$ = 13.8 Hz, 6H, H-1b), 4.60 (q, $^3J_{HH}$ = 1.9 Hz, 4H, H_{Cp}), 4.80 (q, $^3J_{HH}$ = 1.9 Hz, 4H, H_{Cp}), 7.55–7.71 (m, 16H, $H_{o\text{-}Ph}$, $H_{m\text{-}Ph}$), 7.81–7.87 (m, 4H, $H_{p\text{-}Ph}$) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_3CN): δ = 8.5 (d, $^1J_{CP}$ = 60.4 Hz, C-1b), 65.1 (d, $^1J_{CP}$ = 101.6 Hz, $C_{Cp,ipso}$), 75.3 (d, $^{2/3}J_{CP}$ = 12.4 Hz, C_{Cp}), 77.4 (d, $^{2/3}J_{CP}$ = 10.2 Hz, C_{Cp}), CF_3 resonance overlain by CD_3CN-signal, 121.4 (d, $^1J_{CP}$ = 91.0 Hz, $C_{Ph,ipso}$), 131.0 (d, $^2J_{CP}$ = 13.1 Hz, $C_{o\text{-}Ph}$), 133.4 (d, $^3J_{CP}$ = 11.0 Hz, $C_{m\text{-}Ph}$), 136.1 (d, $^4J_{CP}$ = 3.0 Hz, $C_{p\text{-}Ph}$) ppm; ^{19}F NMR (282.4 MHz, CD_3CN): δ = −80.9 ppm. MS (ESI+, MeOH) *m*/*z* (%) = 292.0732 (100, $[M - (NTf_2)_2]^{2+}$ requires 292.0737), 864.0654 (47, $[M - (NTf_2)]^+$ requires 864.0653); MS (ESI−, MeOH) *m*/*z* (%) = 279.9178 (66, $[NTf_2]^-$ requires 279.9178). IR (neat): ν = 3109 (w), 3010 (w), 2932 (w), 1486 (w), 1440 (m), 1420 (w), 1397 (w), 1349 (s), 1179 (vs), 1138 (s), 1111 (s), 1049 (s), 997 (m), 896 (m), 865 (m), 838 (m), 786 (m), 753 (m), 740 (m), 719 (m), 687 (m), 608 (s), 568 (s), 536 (m), 511 (m), 483 (m), 464 (m), 443 (m), 424 (m). $E_{1/2}$ ([EMIM]NTf_2) = 983 mV *vs.* Fc/Fc^+.

Preparation of methyl bis(trifluoromethanesulfonyl)imide (6) MeNTf$_2$. *Method A*: 570 mg methyl iodide (4.02 mmol, 1.0 eq.) was condensed onto 2.00 g silver bis(trifluoromethanesulfonyl)imide (5.15 mmol, 1.3 eq.). The reaction mixture was stirred for 12 h at ambient temperature. The crude product was cleaned by recondensation. The desired product (984 mg, 3.33 mmol, 83%) was achieved as a colorless liquid. *Method B*: 4.76 g silver nitrate (28.0 mmol, 1.11 eq.) was dissolved in a minimum amount acetonitrile and added to 8.04 g lithium bis(trifluoromethanesulfonyl)imide (28.0 mmol, 1.11 eq.) dissolved in a minimum amount acetonitrile. The reaction mixture was stirred at ambient temperature for 2 h and the solvent was removed in a vacuum at 50 °C. The *in situ* generated $[Ag(MeCN)_4]_2[Ag(NTf_2)_3]$ was treated slowly at −78 °C with 3.58 g methyl iodide (25.2 mmol, 1.0 eq.) and stirred at ambient temperature for 12 h. The crude product was cleaned by distillation under ambient pressure to obtain 4.73 g **6** (16.02 mmol, 57%). ^{1}H NMR (300.1 MHz, C_6D_6): δ = 2.61 (s, 3H, Me); $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ = 38.1 (s, Me), 119.4 (q, $^1J_{CF}$ = 324.0 Hz, CF_3); ^{19}F NMR (C_6D_6) δ = −73.9 ppm. IR (neat): ν = 1448 (s), 1419 (s), 1337 (w), 1203 (vs), 1117 (vs), 1042 (m), 834 (vs), 767 (m), 688 (m), 598 (vs), 568 (s), 501 (vs) cm^{-1}.

Preparation of [iron-cyclopentadienyl-η^6-benzene]bis(trifluoromethanesulfonyl)imide (7a) [$(C_5H_5)Fe(\eta^6\text{-}C_6H_6)$]NTf$_2$. 1.48 g ferrocene (7.95 mmol, 1.0 eq.), 4.24 g $AlCl_3$ (33.2 mmol,

4.2 eq.) and 215 mg aluminium powder (7.95 mmol, 1.0 eq.) were suspended in 25 mL benzene and heated to reflux for 1 h. 0.2 mL water (11.1 mmol, 1.4 eq.) was added at ambient temperature and subsequently heated again to reflux for 12 h. The reaction mixture was hydrolysed with 40 mL ice water, filtered and washed three times with 20 mL Et_2O. The aqueous phase was adjusted to an initial pH of 9 using aqueous ammonia, the precipitate was filtered and the solution was treated with an aqueous solution of 2.28 g lithium bis(trifluoromethanesulfonyl)imide (7.95 mmol, 1.0 eq.). The resulting yellow precipitate was filtered and washed with Et_2O and *n*-pentane to obtain 1.57 g $[(C_5H_5)Fe(\eta^6\text{-}C_6H_6)]NTf_2$ (3.07 mmol, 39%). Anal. calc. for $C_{13}H_{11}F_6FeNO_4S_2$ (479.20 g mol^{-1}) C 32.58, H 2.31, N 2.92%; found C 32.69, H 2.27, N 3.10%. ^{1}H NMR (300.1 MHz, acetone-d^6): δ = 5.24 (s, 5H, H_{Cp}), 6.50 (s, 6H, H_{arom}) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, acetone-d^6): δ = 77.61 (s, C_{Cp}), 89.40 (s, C_{arom}) ppm; ^{19}F NMR (282 MHz, acetone-d^6): δ = −78.9 ppm. MS (ESI+, MeOH) *m*/*z* (%) = 199.0205 (100, $[M - NTf_2]^+$ requires 199.0205); MS (ESI−, MeOH) *m*/*z* (%) = 279.9179 (60, $[NTf_2]^-$ requires 279.9178). IR (neat): ν = 3116 (w), 3093 (w), 1450 (w), 1422 (w), 1348 (s), 1333 (s), 1177 (s), 1134 (s), 1050 (s), 918 (w), 856 (m), 828 (m), 788 (m), 762 (w), 739 (m), 610 (s), 568 (s), 512 (s), 468 (s), 408 (w) cm^{-1}.

Preparation of tributylcyclopentadienylidene phosphorane (8b). *Method A*: 1.00 g sodium cyclopentadienide (11.35 mmol, 1.2 eq.) was suspended in 60 mL *n*-hexane and treated at 0 °C with 1.71 g **1b** (9.46 mmol, 1.0 eq.). After stirring for 12 h at ambient temperature the resulting suspension was treated at 0 °C with 3.7 mL *n*-butyllithium (2.55M in *n*-hexane, 9.46 mmol, 1.0 eq.) and after stirring for 6 h at 0 °C the reaction mixture was treated with 1.94 g 1-bromobutane (14.19 mmol, 1.5 eq.). The suspension was stirred for 1 d at ambient temperature and after filtration and extraction with four times 10 mL *n*-hexane and removing the solvent in a vacuum 1.97 g **8b** (7.40 mmol, 78%) was obtained. *Method B*: 948 mg **10** (3.82 mmol, 1.0 eq.) was suspended in 30 mL Et_2O and treated with 576 mg 1-bromobutane (4.20 mmol, 1.1 eq.). After stirring for 1 d at ambient temperature the reaction mixture was filtered using a syringe filter (Phenex, PTFE; pore size: 0.45 μm). The solvent was removed in a vacuum to obtain 835 mg **8b** (3.13 mmol, 82%). Anal. calc. for $C_{17}H_{31}P$ (266.40 g mol^{-1}) C 76.64, H 11.73%; found C 76.42, H 11.51%. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 13.6 ppm; ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 0.96 (t, $^3J_{HH}$ = 7.2 Hz, 9H, $P(CH_2)_3\mathit{Me}$), 1.41–1.50 (m, 6H, $P(CH_2)_2CH_2Me$), 1.52–1.62 (m, 6H, PCH_2CH_2Et), 1.98–2.08 (m, 6H, $PCH_2{}^nPr$), 6.28–6.31 (m, 2H, H_{Cp}), 6.33–6.36 (m, 2H, H_{Cp}) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 13.4 (s, $P(CH_2)_3\mathit{Me}$), 23.1 (d, $^1J_{CP}$ = 54.2 Hz, $PCH_2{}^nPr$), 24.0 (s, $P(CH_2)_2CH_2Me$), 24.1 (d, $^2J_{CP}$ = 10.5 Hz, PCH_2CH_2Et), 79.2 (d, $^1J_{CP}$ = 105.0 Hz, $C_{Cp,ipso}$), 112.1 (d, $^{2/3}J_{CP}$ = 14.5 Hz, C_{Cp}), 112.8 (d, $^{2/3}J_{CP}$ = 16.7 Hz, C_{Cp}) ppm. MS (EI+) *m*/*z* = 266.2169 ($C_{17}H_{31}P$ requires 266.2163); MS (ESI+, MeOH) *m*/*z* (%) = 267.2236 (100, $[M + H]^+$ requires 267.2236). IR (neat): ν = 3067 (w), 2956 (m), 2928 (m), 2870 (m), 1463 (m), 1437 (m), 1409 (w), 1378 (w), 1345 (w), 1276 (w), 1225 (m), 1094 (m), 1037 (s), 1007 (m), 969 (w), 889 (m), 791 (m), 701 (s), 612 (m), 531 (w), 504 (m), 469 (m), 441 (w) cm^{-1}.

Preparation of dibutylcyclopentadienyl phosphine (9). 1.72 g sodium cyclopentadienide (19.53 mmol, 1.2 eq.) was suspended in 100 mL *n*-pentane and treated at 0 °C with 2.93 g **1b** (16.22 mmol, 1.0 eq.). After stirring at ambient temperature for 12 h the volume was reduced to half the original volume and filtered. The residue was extracted two times with 20 mL *n*-pentane and after removing the solvent in a vacuum 2.96 g **9** (14.08 mmol, 87%) was obtained as a slightly yellow oil. **9** was isolated as a mixture of three isomers. *Dibutylcyclopenta-2,4-dienyl phosphine*: $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ = −20.8 ppm (4%); ^{1}H NMR (300.1 MHz, C_6D_6): δ = 0.83 (t, $^3J_{HH}$ = 7.0 Hz, 6H, $P(CH_2)_3\mathit{Me}$), 1.27–1.43 (m, 8H, $P(CH_2)_2CH_2Me$, PCH_2CH_2Et), 1.45–1.60 (m, 4H, $PCH_2{}^nPr$), 3.39–3.42 (m, 1H, $H_{Cp,ipso}$), 6.46–6.50 (m, 4H, H_α, H_β) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ = 14.0 (s, $P(CH_2)_3\mathit{Me}$), 26.3 (d, $^3J_{CP}$ = 17.7 Hz, $P(CH_2)_2CH_2Me$), 28.0 (d, $^1J_{CP}$ = 11.4 Hz, $PCH_2{}^nPr$), 29.4 (d, $^2J_{CP}$ = 16.8 Hz, PCH_2CH_2Et), 52.7 (d, $^1J_{CP}$ = 24.0 Hz, $C_{Cp,ipso}$), 132.0 (d, $^3J_{CP}$ = 3.4 Hz, C_β), 135.1 (d, $^2J_{CP}$ = 4.8 Hz, C_α) ppm. *Dibutylcyclopenta-1,4-dienyl phosphine*: $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ = −37.5 ppm (68%); ^{1}H NMR (300.1 MHz, C_6D_6): δ = 0.83 (t, $^3J_{HH}$ = 7.0 Hz, 6H, $P(CH_2)_3\mathit{Me}$), 1.27–1.43 (m, 8H, $P(CH_2)_2CH_2Me$, PCH_2CH_2Et), 1.45–1.60 (m, 4H, $PCH_2{}^nPr$), 2.84–2.87 (m, 2H, $C_\beta H_2$), 6.42–6.44 (m, 2H, $C_\alpha H$), 6.76–6.80 (dquint, $^3J_{PH}$ = 5.0 Hz, $^{2/3}J_{HH}$ = 1.5 Hz, $C_\beta H$) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ = 14.0 (s, $P(CH_2)_3\mathit{Me}$), 24.7 (d, $^3J_{CP}$ = 11.6 Hz, $P(CH_2)_2CH_2Me$), 28.3 (d, $^1J_{CP}$ = 11.0 Hz, $PCH_2{}^nPr$), 28.9 (d, $^2J_{CP}$ = 14.1 Hz, PCH_2CH_2Et), 42.8 (d, $^3J_{CP}$ = 5.0 Hz, $C_{Cp}H_2$), 133.1 (d, $^2J_{CP}$ = 8.0 Hz, C_α), 136.4 (d, $^2J_{CP}$ = 2.1 Hz, C_α), 140.2 (d, $^3J_{CP}$ = 25.2 Hz, C_β), 147.0 (d, $^1J_{CP}$ = 19.7 Hz, $C_{Cp,ipso}$) ppm. *Dibutylcyclopenta-1,3-dienyl phosphine*: $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ = −40.3 ppm (28%); ^{1}H NMR (300.1 MHz, C_6D_6): δ = 0.83 (t, $^3J_{HH}$ = 7.0 Hz, 6H, $P(CH_2)_3\mathit{Me}$), 1.27–1.43 (m, 8H, $P(CH_2)_2CH_2Me$, PCH_2CH_2Et), 1.45–1.60 (m, 4H, $PCH_2{}^nPr$), 2.74–2.78 (m, 2H, $C_\alpha H_2$) 6.30–6.35 (m, 1H, $C_\alpha H$), 6.52–6.57 (m, 1H, $C_\beta H$), 6.59–6.64 (m, 1H, $C_\beta H$) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ = 14.0 (s, $P(CH_2)_3\mathit{Me}$), 24.7 (d, $^3J_{CP}$ = 11.6 Hz, $P(CH_2)_2CH_2Me$), 27.2 (d, $^1J_{CP}$ = 11.1 Hz, $PCH_2{}^nPr$), 28.8 (d, $^2J_{CP}$ = 13.8 Hz, PCH_2CH_2Et), 43.1 (d, $^2J_{CP}$ = 7.1 Hz, $C_\alpha H_2$), 133.5 (d, $^3J_{CP}$ = 7.6 Hz, $C_\beta H$), 133.8 (d, $^2J_{CP}$ = 3.3 Hz, $C_\alpha H$), 139.6 (d, $^3J_{CP}$ = 23.1 Hz, $C_\beta H$), 145.3 (d, $^1J_{CP}$ = 18.0 Hz, $C_{Cp,ipso}$) ppm. MS (EI+) *m*/*z* = 210.1539 ($C_{13}H_{23}P$ requires 210.1537). IR (neat): ν = 3091 (w), 3070 (w), 2956 (s), 2925 (s), 2871 (m), 2858 (m), 1463 (m), 1416 (m), 1375 (m), 1345 (m), 1295 (w), 1260 (w), 1221 (w), 1199 (w), 1092 (m), 1066 (m), 993 (m), 968 (w), 948 (m), 928 (w), 893 (s), 863 (w), 841 (vw), 810 (m), 788 (m), 717 (m), 678 (s), 585 (m), 463 (w), 436 (w) cm^{-1}.

Preparation of potassium dibutylphosphinocyclopentadienide (10). 968 mg **9** (4.60 mmol, 1.0 eq.) was dissolved in 20 mL Et_2O and treated in portions at 0 °C with 599 mg benzyl potassium (4.60 mmol, 1.0 eq.). After complete addition of benzyl potassium the color of the reaction mixture turned from dark red to slightly orange and a slightly orange precipitate was

formed. The residue was filtrated and washed two times with 10 mL Et_2O and two times with 20 mL *n*-pentane. After drying 948 mg **10** (3.82 mmol, 83%) obtained as a colorless solid. $^{31}P\{^1H\}$ NMR (121.5 MHz, THF-d^8): δ = −38.6 ppm; ^1H NMR (300.1 MHz, THF-d^8): δ = 0.93 (t, $^3J_{HH}$ = 6.9 Hz, 6H, $P(CH_2)_3\mathit{Me}$), 1.29–1.58 (m, 12H, $P(CH_2)_2CH_2Me$, PCH_2CH_2Et, $PCH_2{}^nPr$), 5.64–5.69 (m, 2H, H_{Cp}), 5.76–5.81 (m, 2H, H_{Cp}) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, THF-d^8): δ = 15.1 (s, $P(CH_2)_3\mathit{Me}$), 26.2 (d, $^3J_{CP}$ = 11.6 Hz, $P(CH_2)_2CH_2Me$), 31.0 (d, $^1J_{CP}$ = 16.1 Hz, $PCH_2{}^nPr$), 32.7 (d, $^2J_{CP}$ = 11.7 Hz, PCH_2CH_2Et), 108.1 (d, $^{2/3}J_{CP}$ = 7.9 Hz, C_{Cp}), 111.5 (d, $^{2/3}J_{CP}$ = 18.7 Hz, C_{Cp}), 111.8 (d, $^1J_{CP}$ = 1.8 Hz, $C_{Cp,\mathit{ipso}}$) ppm. IR (neat): ν = 3059 (w), 2956 (m), 2923 (m), 2871 (m), 2856 (m), 1463 (m), 1432 (m), 1377 (w), 1343 (w), 1202 (w), 1178 (w), 1092 (w), 1029 (m), 967 (w), 889 (w), 779 (m), 729 (s), 716 (s), 644 (m), 496 (w), 472 (m), 446 (w), 425 (w) cm^{-1}.

(1-Ferrocenylethyl)tributylphosphonium bis(trifluoromethanesulfonyl)imide (11) [FcCHMePBu$_3$]NTf$_2$. 350 mg 1-hydroxyethylferrocene (1.52 mmol, 1.0 eq.) was dissolved in 20 mL chloroform and treated with 430 mg tributylphosphine hydrobromide (1.52 mmol, 1.0 eq.) and heated to reflux for 2 h. Subsequently the solvent was removed in a vacuum. The residue was washed two times with 10 mL Et_2O and two times with 20 mL *n*-pentane. After drying (1-ferrocenylethyl)tributylphosphonium bromide was obtained as a orange oil. The bromide and 479 mg $LiNTf_2$ (1.67 mmol, 1.1 eq.) were suspended in a water–methanol mixture (20 mL, 1 : 1) and stirred at 40 °C for 1 d. The reaction mixture was extracted with 20 mL portions of DCM until the organic phase does not turn orange. The solvent was removed in a vacuum and the received crude product was washed two times with 10 mL Et_2O. After drying 681 mg **11** (0.98 mmol, 64%) was obtained as a orange oil which solidified after several months. Anal. calc. for $C_{26}H_{40}F_6FeNO_4PS_2$ (695.54 g mol^{-1}) C 44.90, H 5.80, N 2.01%; found C 45.17, H 6.15, N 2.07%. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 34.7 ppm; ^1H NMR (300.1 MHz, $CDCl_3$): δ = 0.93 (t, $^3J_{HH}$ = 7.0 Hz, 9H, $P(CH_2)_3\mathit{Me}$), 1.36–1.48 (m, 12H, $P(CH_2)_2CH_2Me$, PCH_2CH_2Et), 1.74 (dd, $^2J_{PH}$ = 16.9 Hz, $^3J_{HH}$ = 7.1 Hz, 3H, $CH\mathit{Me}$), 1.94–2.00 (m, 6H, $PCH_2{}^nPr$), 3.51–3.58 (m, 1H, CHMe), 4.10 (s, 1H, H_α), 4.25 (s, 6H, H_α, $H_{Cp'}$), 4.28 (s, 1H, H_β), 4.30 (s, 1H, H_β) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 13.1 (s, $P(CH_2)_3\mathit{Me}$), 14.2 (s, $CH\mathit{Me}$), 17.3 (d, $^1J_{CP}$ = 44.7 Hz, $PCH_2{}^nPr$), 23.6 (d, $^3J_{CP}$ = 5.0 Hz, $P(CH_2)_2CH_2Me$), 23.9 (d, $^2J_{CP}$ = 14.9 Hz, PCH_2CH_2Et), 27.9 (d, $^1J_{CP}$ = 41.5 Hz, CHMe), 66.0 (d, $^3J_{CP}$ = 0.9 Hz, C_α), 68.8 (d, $^3J_{CP}$ = 1.3 Hz, C_α), 69.0 (s, C_β), 69.1 (s, C_β), 69.4 (s, $C_{Cp'}$), 82.8 (s, $C_{Cp,\mathit{ipso}}$), 120.0 (q, $^1J_{CF}$ = 321.6 Hz, CF_3) ppm; ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = −79.2 ppm. MS (ESI+, MeOH) *m*/*z* (%) = 415.2211 (15, $[M-(NTf_2)]^+$ requires 415.2212), 213.0361 (100, $[FcCHMe]^+$ requires 213.0361); MS (ESI−, MeOH) *m*/*z* (%) = 279.9179 (90, $[NTf_2]^-$ requires 279.9178). IR (neat): ν = 3099 (w), 2962 (m), 2936 (m), 2876 (m), 1466 (m), 1411 (w), 1383 (w), 1348 (s), 1330 (s), 1225 (m), 1177 (vs), 1134 (s), 1105 (m), 1051 (s), 1002 (m), 968 (w), 903 (m), 821 (m), 786 (m), 761 (w), 738 (m), 652 (m), 614 (s), 599 (s), 569 (s), 507 (s), 483 (m), 431 (m). $E_{1/2}$ ([EMIM]NTf_2) = 164 mV *vs.* Fc/Fc^+.

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