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New (1-Phosphanylferrocen-1′- and -2-yl)methyl-Linked Diaminocarbene Ligands: Synthesis and Rhodium(I) Complexes

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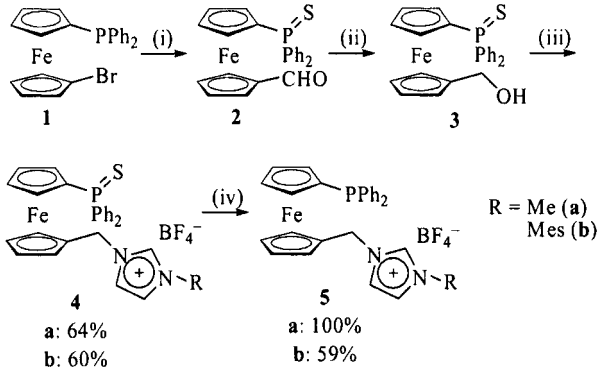
Two ferrocenylmethanols, [1′-(diphenylthiophosphanyl)-ferrocen-1-yl]methanol (**3**) and [2-(diphenylthiophosphanyl)-ferrocen-1-yl]methanol (**6**), have been converted in one step into the 1,1′- and 1,2-ferrocenediyl-linked thiophosphane/*N*-R-imidazolium salts **4a**,**b** and **7a**,**b** (**a**: R = Me; **b**: R = 2,4,6-$Me_3C_6H_2$ or Mes). This straightforward method allows the linkage of an imidazolium group to a ferrocene unit with a nonsubstituted methylene bridge. After desulfurisation of the phosphane group, the ligands reacted with an Rh^I precursor, in the presence of *t*BuOK, to give cationic complexes **9a**,**b** and **10a**,**b**. All compounds were characterised by elemental analysis, NMR spectroscopy and mass spectrometry. The molecular structures of compounds **4a**, **7a** and **9a** were determined by X-ray crystallography.

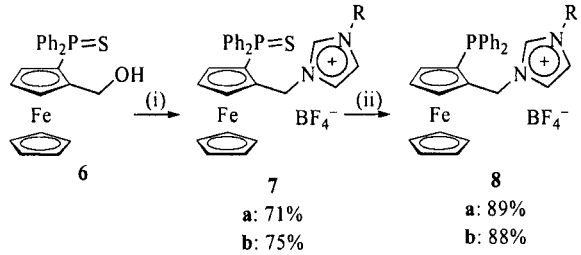
The chemistry of N-heterocyclic carbenes (NHCs) has experienced a very rapid development over the past ten years.[1] They have found many applications in catalysis, since the corresponding transition metal complexes have proven to be very active, robust and generally air-stable.[2] Ligands associating an NHC and a phosphane have also shown very interesting properties,[3] in particular for C–C coupling reactions catalysed by palladium or nickel.[4]

To date, there are only two synthetic methods allowing the preparation of ferrocenediyl-linked phosphane/NHC ligands with an aryl (or ferrocenyl) substituent on the imidazole moiety.[5,6] However, the carbon atom situated in α-position to the Cp ring has a methyl substituent in both cases. To the best of our knowledge, there is no precedent in the literature for 1,1′-disubstituted ferrocenediyl phosphane/imidazolium ligands. On the other hand, the fundamental difference between our 1,2-disubstituted ligands and previously reported ligands is that the former possess only planar chirality, whereas the latter have both planar and central chirality.[5,6] Thus, it becomes possible to study the specific effect of planar chirality in asymmetric catalytic reactions. We present here a new synthetic method for 1,1′- and racemic 1,2-disubstituted ferrocenediyl phosphane/imidazolium ligands, which are precursors of phosphane/NHCs.

The precursors for the introduction of the imidazolium moiety are alcohols **3** (Scheme 1) and **6** (Scheme 2). The synthesis of racemic (as well as enantiomerically pure) alcohol **6** is already well known.[7,8] We have adapted this method to prepare the new alcohol **3**. It was successfully obtained in two steps from known 1-bromo-1′-(diphenylphosphanyl)ferrocene,[9] with satisfactory yields.



Scheme 1. Synthesis of 1,1′-ferrocenediyl ligands. i. a) *n*BuLi, THF, –25 °C, b) dmf, –25 °C, c) S_8, CH_2Cl_2, 40 °C (70%); ii. $NaBH_4$, toluene/NaOH, 0 °C (88%); iii. a) HBF_4, CH_2Cl_2, room temp., b) *N*-R-imidazole; iv) Raney Ni, MeCN, room temp. or 80 °C.



Scheme 2. Synthesis of 1,2-ferrocenediyl ligands. i. a) HBF_4, CH_2Cl_2, room temp., b) *N*-R-imidazole; ii) Raney Ni, MeCN, room temp. or 80 °C.

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Procedures for introducing an *N*-substituted imidazole ring on a ferrocenyl unit can involve the displacement of a chloride,[10] an acetate,[6,11] or a dimethylamino group.[5] Bolm et al. described the efficient conversion of ferrocenyl alcohols into corresponding imidazolium compounds by a two-step procedure.[12,13] However, this method has not been applied so far to introduce aryl or tertiary alkyl groups. Here, the imidazolium functionality has been introduced in one-pot procedure from the alcohol, according to a protocol developed earlier in our group for the introduction of various nucleophiles on 1,2-disubstituted ferrocenediyl phosphanes.[14] The α-carbocation is generated with a strong acid and reacts with the *N*-R-imidazole (**a**: R = Me; **b**: R = 2,4,6-$Me_3C_6H_2$ or Mes). This method allowed us to introduce equally well imidazolium groups bearing a primary alkyl or an aryl substituent. The reactions are clean, very rapid and high-yielding (Schemes 1 and 2).[15] The structure of the intermediates **4a** and **7a** was confirmed by X-ray diffraction methods (Figure 1). The bond lengths and angles in both compounds are all within the expected range. The imidazolium moiety is *exo* with respect to the ferrocene unit, and slightly tilted towards the diphenylphosphanyl group in the case of **7a**. In **4a**, the packing is governed by C–H···π interactions involving the H(64) atom of the imidazolium group and the centroid of the symmetry-related Cp ring bearing the imidazolium group [C(64)–H(64)···Cg2^{i}: C(64)–H(64) 0.95 Å; H(64)···Cg2^{i} 2.74 Å; C(64)···Cg2^{i} 3.562(5) Å; C(64)–H(64)···Cg2^{i} 144.8°; symmetry code (i): $-x + 1, -y + 1, -z + 1$], leading to the formation of a centrosymmetric pseudo dimer. The two molecules within the asymmetric unit in **7a** are also connected through weak C–H···π interactions involving the H(14) atom of the substituted Cp ring of one molecule and the centroid of the C(211)–C(216) phenyl ring of the other one [C(14)–H(14)···Cg3: C(14)–H(14) 0.93 Å; H(14)···Cg3 3.13 Å; C(14)···Cg3 3.755(3) Å; C(14)–H(14)···Cg3 126.5°]. In **7a**, the imidazolium ring and one of the phenyl rings [C(121)–C(126); C(221)–C(226)] interact through an offset π–π stacking with a plane-to-plane distance of 3.566(2) Å [3.438(2) Å], a centroid-to-centroid distance of 3.9217(3) Å [3.6301(3) Å] and an offset angle of 24.6° [18.7°]. The sulfur atom in **7a** is pointing towards the iron atom, as has been seen with similar 1,2-disubstituted ferrocenediyl ligands.[8]

Mild reaction conditions were then required for the phosphane deprotection, compatible with the imidazolium moiety. After several attempts, we found that the use of Raney nickel in acetonitrile gave the best results.[16]

(Carbene)rhodium(I) complexes were obtained by deprotonation of the imidazolium salts in the presence of potassium *tert*-butoxide and $[RhCl(cod)]_2$ in THF, followed by chloride abstraction (Scheme 3). The latter step could be carried out with either $NaBF_4$ in CH_2Cl_2/H_2O, or $AgBF_4$ in CH_2Cl_2. The silver reagent results in a faster abstraction process while it does not oxidize the ferrocene unit. Room-temperature conditions for the deprotonation step resulted in good yields (75%) for product **9a**, but less satisfactory results were obtained in other cases (i.e. 32% for **10b**). However, carrying out the deprotonation at –78 °C raised the yield of **10b** to 77%. This shows that the bulky imidazolium substituent does not negatively affect the coordination process. Good yields (81%) were also obtained for **9b** when using the low temperature deprotonation protocol, whereas the yield of **9a** was lowered (62%). While the products with the 1,1′-disubstituted ligands, **9a**,**b**, were obtained selec-

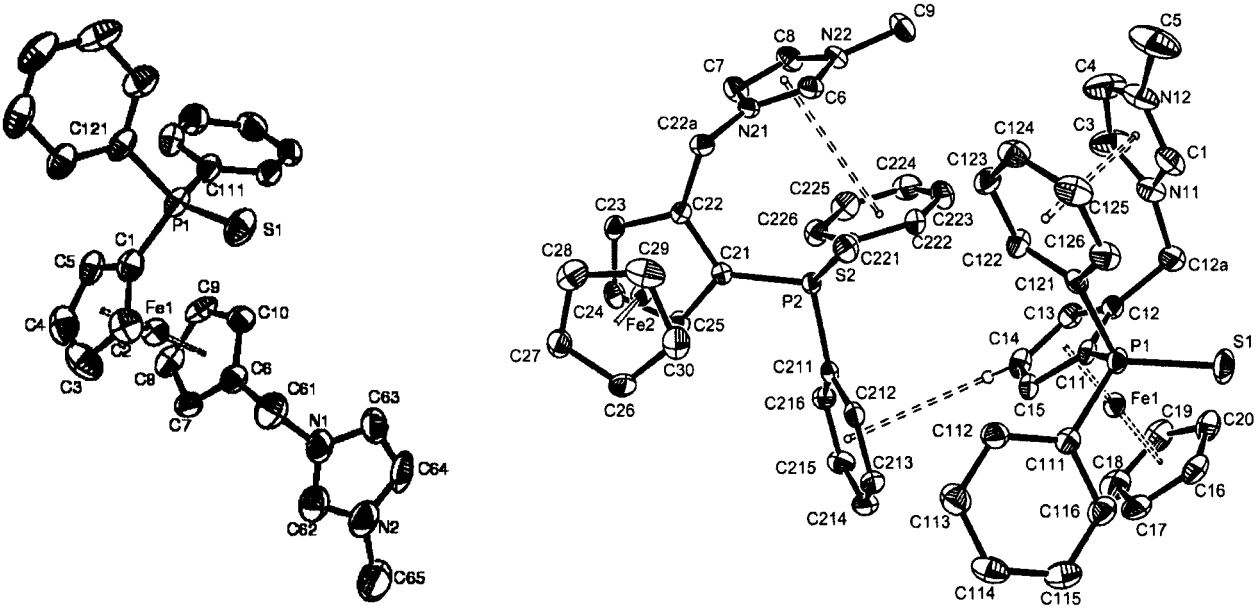
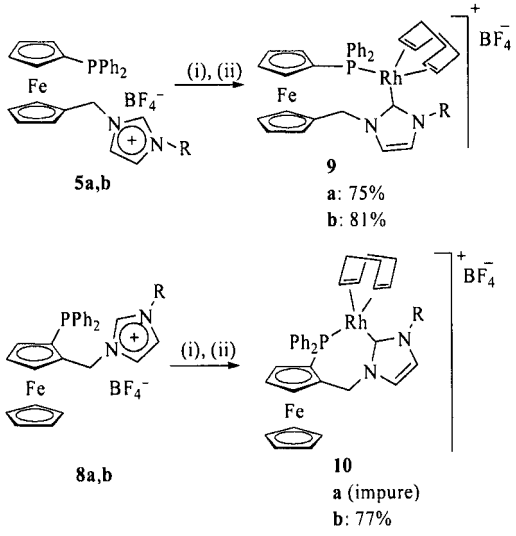


Figure 1. Molecular views of compounds **4a** (left) and **7a** (right) with atom labelling scheme. Ellipsoids are plotted at the 50% level. H atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: **4a**: C(1)–P(1) 1.790(3), C(62)–N(1) 1.324(5), C(62)–N(2) 1.313(5), C(63)–C(64) 1.330(6); N(2)–C(62)–N(1) 108.6(3); **7a**: C(11)–P(1) 1.792(3), C(1)–N(11) 1.317(3), C(1)–N(12) 1.309(4), C(3)–C(4) 1.333(5); N(11)–C(1)–N(12) 109.7(3); C(21)–P(2) 1.801(3), C(6)–N(21) 1.316(3), C(6)–N(22) 1.323(3), C(7)–C(8) 1.344(4); N(21)–C(6)–N(22) 109.4(3).

tively, the reactions with the 1,2-disubstituted ligands yielded by-products. The selectivity for **10b** was almost total,[17] however, complex **10a** was obtained along with another carbene/phosphane complex in a 85:15 ratio.[18,19] It is reasonable to think that, in the case of 1,2-disubstituted ligands, the selectivity is affected by the steric encumbrance of the imidazolium substituent. All complexes are stable in air and could be purified by filtration through silica gel. The structure of complex **9a** was confirmed by X-ray diffraction methods (see Figure 2). The structure shows a square-planar geometry with the carbene and phosphane donors in a *cis* arrangement. The bond lengths and angles are again within the expected range for this kind of complexes. The Rh–carbene distance is in accordance with what Seo obtained with a very similar complex, although the Rh–P distance is slightly longer in our case [2.3345(8) Å instead of 2.2935(10) Å in Seo's Rh^I complex, which has two NHC/phosphane ligands coordinated to the metal centre].[5] However, we do not observe any significant lenghtening of the Rh–C bonds *trans* to the carbene [Rh(1)–CG1], with respect to the other Rh–C bonds [Rh(1)–CG2], as is commonly observed for bifunctional NHC ligands.[5,13] Finally, no tilting of the Cp rings can be observed upon complexation of the ligand to the rhodium centre [the angles between the two least-squares Cp planes are 4.66(29)° for **4a** and 3.15(24)° for **9a**].



Scheme 3. Synthesis of Rh complexes. i. *t*BuOK, $[Rh(cod)Cl]_2$, THF; ii. $NaBF_4$, CH_2Cl_2/H_2O, room temp. or $AgBF_4$, CH_2Cl_2, room temp.

Preliminary tests have been carried out to evaluate the activity of complexes **9a**, **9b** and **10b** (racemic mixture) for the hydrosilylation of ketones. The reaction of diphenylsilane with acetophenone was carried out in dichloromethane or THF at room temperature, with 2 mol-% of catalyst (Table 1). The first results show that THF is a better solvent, despite the low solubility of complexes **9a** and **9b**, and that the complex bearing a 1,2-disubstituted ligand is more active. All complexes show a moderate activity, compared with other literature benchmarks.[13,20]

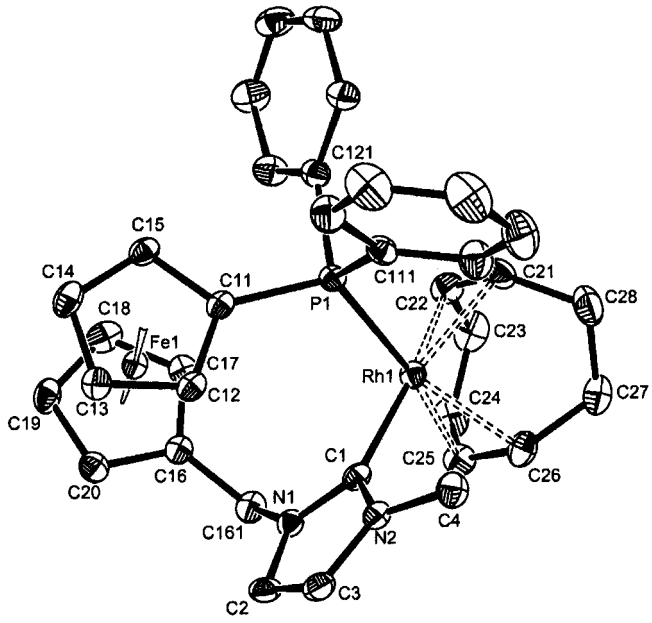


Figure 2. Molecular view of compound **9a** with atom labelling scheme. Ellipsoids are plotted at the 50% level. H atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Rh(1)–C(1) 2.047(3), Rh(1)–P(1) 2.3345(8), Rh(1)–C(21) 2.215(3), Rh(1)–C(22) 2.231(3), Rh(1)–C(25) 2.220(3), Rh(1)–C(26) 2.217(3), Rh(1)–CG1 2.1140(3), Rh(1)–CG2 2.1091(3), N(1)–C(1) 1.359(4), N(2)–C(1) 1.357(4), C(2)–C(3) 1.338(4); C(1)–Rh(1)–P(1) 90.83(8), C(1)–Rh(1)–CG1 175.91(8), C(1)–Rh(1)–CG2 90.46(8), CG1–Rh(1)–P(1) 93.26(2), CG2–Rh(1)–P(1) 174.69(2), CG2–Rh(1)–CG1 85.450(10), N(1)–C(2)–N(2) 104.5(2). CG1 and CG2 denote the C(21)–C(22) centroid and the C(25)–C(26) centroid, respectively.

Table 1. Hydrosilylation of acetophenone with diphenylsilane. Conditions: 1 equiv. of acetophenone, 1.1 equiv. of diphenylsilane, 2 mol-% of catalyst, room temperature.

Entry	Complex	Solvent	*t* (d)	Conversion (%)[a]
1	**9a**	CH_2Cl_2	7	17
2	**9a**	THF	3	46
3	**9b**	THF	3	49
4	**10b**	THF	3	67

[a] Determined by ^1H NMR spectroscopy after hydrolysis of the silylated intermediate.

In conclusion, we have prepared new ferrocenediyl phosphane/imidazolium ligands by a general and effective method. Further tests will be carried out to evaluate the activity of the Rh^I complexes in various catalytic reactions. Enantiomerically pure 1,2-disubstituted ligands will also be prepared and tested in the asymmetric version of the reactions. Results will be published in due course.

Experimental Section

General: All reactions were carried out under dry argon using Schlenk glassware and vacuum-line techniques. Solvents for syntheses were dried and degassed by standard methods before use. *N*,*N*-Dimethylformamide (dmf) was purified by distillation from CaH_2. Spectra were recorded with a Bruker AM250, a Bruker AV300 or a Bruker AV500 spectrometer. All spectra were recorded in $CDCl_3$,

unless otherwise stated. Mass spectra were obtained from acetonitrile solutions with a TSQ7000 instrument from ThermoElectron. All new compounds described were fully characterised by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, elemental analysis and mass spectrometry. 1,1′-dibromoferrocene and 1-bromo-1′-(diphenylphosphanyl)-ferrocene were prepared according to literature procedures.[9]

General Procedures for the Preparation of Imidazolium Salts: To a solution of **3** (100 mg, 0.23 mmol) in degassed dichloromethane (5 mL) was quickly added HBF_4 (35 μL, 54 wt-% in Et_2O), immediately followed by an *N*-substituted imidazole (0.35 mmol). The mixture was washed with 2 M aq. HCl, water, satd. aq. $NaHCO_3$ and water again. The organic phase was dried ($MgSO_4$), filtered and concentrated in vacuo. Methyl-substituted salts: the residue was taken up in dichloromethane (1 mL), diethyl ether was added and the orange precipitate was filtered, washed with diethyl ether and dried in vacuo to give a yellow-orange solid. Mesityl-substituted salts: the residue was purified by column chromatography on silica gel (eluent: CH_2Cl_2/acetone, 9:1) to give a yellow-orange solid. Similar yields were obtained starting from 500 mg of **3**.

Imidazolium Salt 4a: 86 mg, 64% yield. Single crystals suitable for X-ray diffraction studies were obtained by slow concentration of a dichloromethane solution. $C_{27}H_{26}BF_4FeN_2PS$ (584.21): calcd. C 55.51, H 4.49, N 4.80; found C 54.98, H 4.16, N 4.55. ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ = 8.65 (s, 1 H, NC*H*N$^+$), 7.79–7.72 (m, 4 H, PPh_2), 7.59–7.47 (m, 6 H, PPh_2), 7.29 (s, 1 H, HC=C Im$^+$), 7.27 (s, 1 H, HC=C Im$^+$), 5.09 (s, 2 H, Cp), 4.69 (s, 2 H, Cp), 4.54 (s, 2 H, Cp or CH_2Im$^+$), 4.50 (s, 2 H, Cp or CH_2Im$^+$), 4.16 (s, 2 H, Cp), 3.88 (s, 3 H, CH_3Im$^+$) ppm. $^{13}C\{^{1}H\}$ NMR (75.5 MHz, CD_2Cl_2, 25 °C): δ = 135.5 (NCN$^+$), 134.2 (d, $J_{P,C}$ = 87.0 Hz, 2× quat. PPh_2), 131.55 (2× PPh_2), 131.53 (d, $J_{P,C}$ = 10.6 Hz, 4× PPh_2), 128.4 (d, $J_{P,C}$ = 12.5 Hz, 4× PPh_2), 123.6 (C=C Im$^+$), 121.8 (C=C Im$^+$), 80.4 (quat. Cp^C), 76.2 (d, $J_{P,C}$ = 96.9 Hz, quat. Cp^P), 74.1 (d, $J_{P,C}$ = 12.4 Hz, 2× Cp^P), 73.1 (d, $J_{P,C}$ = 10.0 Hz, 2× Cp^P), 71.7 (2× Cp^C), 71.3 (2× Cp^C), 49.1 (*C*H_2Im$^+$), 36.3 (*C*H_3Im$^+$) ppm. $^{31}P\{^{1}H\}$ NMR (81.0 MHz, CD_2Cl_2, 25 °C): δ = 41.0 ppm. MS (ESI): *m*/*z* (%) = 497 (70) [M$^+$], 415 (100) [M$^+$ – $C_4H_6N_2$].

Imidazolium Salt 4b: 96 mg, 60% yield. $C_{35}H_{34}BF_4FeN_2PS$ (688.36): calcd. C 61.07, H 4.98, N 4.07; found C 60.31, H 4.71, N 3.91. ^{1}H NMR (300 MHz, CD_3CN, 25 °C): δ = 8.54 (s, 1 H, NC*H*N$^+$), 7.80–7.73 (m, 4 H, PPh_2), 7.60–7.50 (m, 7 H, PPh_2 + HC=C Im$^+$), 7.40 (s, 1 H, HC=C Im$^+$), 7.11 (s, 2 H, Mes), 5.15 (br. s, 2 H, CH_2Im$^+$), 4.71 (br. s, 2 H, Cp), 4.55 (br. s, 2 H, Cp), 4.51 (br. s, 2 H, Cp), 4.18 (br. s, 2 H, Cp), 2.36 (s, 3 H, *p*-CH_3 Mes), 2.00 (s, 6 H, *o*-CH_3 Mes) ppm. $^{13}C\{^{1}H\}$ NMR (75.5 MHz, CD_3CN, 25 °C): δ = 141.2 (quat. Mes), 135.8 (NCN$^+$), 134.7 (2× quat. Mes), 134.4 (d, $J_{P,C}$ = 87.0 Hz, 2× quat. PPh_2), 131.7 (d, $J_{P,C}$ = 2.9 Hz, 2× PPh_2), 131.4 (d, $J_{P,C}$ = 10.7 Hz, 4× PPh_2), 131.0 (quat. Mes), 129.5 (2× C-H Mes), 128.5 (d, $J_{P,C}$ = 12.5 Hz, 4× PPh_2), 124.2 (C=C Im$^+$), 122.7 (C=C Im$^+$), 80.7 (quat. Cp^C), 76.1 (d, $J_{P,C}$ = 97.3 Hz, quat. Cp^P), 74.0 (d, $J_{P,C}$ = 12.4 Hz, 2× Cp^P), 73.2 (d, $J_{P,C}$ = 10.1 Hz, 2× Cp^P), 71.6 (2× Cp^C), 71.2 (2× Cp^C), 49.2 (*C*H_2Im$^+$), 20.2 (*p*-CH_3 Mes), 16.6 (2× *o*-CH_3 Mes) ppm. $^{31}P\{^{1}H\}$ NMR (121.5 MHz, CD_3CN, 25 °C): δ = 40.6 ppm. MS (ESI): *m*/*z* (%) = 601 (100) [M$^+$], 415 (100) [M$^+$ – $C_{12}H_{14}N_2$].

Imidazolium Salt 7a: 96 mg, 71% yield. Single crystals suitable for X-ray diffraction studies were obtained by slow diffusion of diethyl ether into a THF solution. $C_{27}H_{26}BF_4FeN_2PS$ (584.21): calcd. C 55.51, H 4.49, N 4.80; found C 51.53, H 3.90, N 4.32. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 8.33 (s, 1 H, NC*H*N$^+$), 7.73–7.33 (m, 10 H, PPh_2), 6.98 (br. s, 1 H, HC=C Im$^+$), 6.87 (br. s, 1 H, HC=C Im$^+$), 6.41 (br. s, 1 H, CH_2Im$^+$), 5.15–5.04 (m, 2 H, CH_2Im$^+$ + Cp), 4.52 (br. s, 1 H, Cp), 4.41 (br. s, 5 H, Cp′), 3.81 (br. s, 1 H, Cp), 3.52 (br. s, 3 H, CH_3Im$^+$) ppm. $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 135.9 (NCN$^+$), 134.0 (d, $J_{P,C}$ = 85.6 Hz, 2× quat. PPh_2), 132.2–131.8 (m, 5× PPh_2), 131.4 (d, $J_{P,C}$ = 10.1 Hz, 2× PPh_2), 128.7 (d, $J_{P,C}$ = 12.6 Hz, PPh_2), 128.45 (d, $J_{P,C}$ = 12.6 Hz, 2× PPh_2), 123.6 (C=C, Im$^+$), 122.4 (C=C, Im$^+$), 83.4 (d, $J_{P,C}$ = 11.3 Hz, quat. Cp), 77.5–77.0 (Cp + $CDCl_3$), 76.3 (d, $J_{P,C}$ = 11.3 Hz, Cp), 74.3 (d, $J_{P,C}$ = 94.4 Hz, quat. Cp), 71.4 (Cp′), 71.3 (Cp), 48.2 (*C*H_2Im$^+$), 37.0 (*C*H_3Im$^+$) ppm. $^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$, 25 °C): δ = 40.7 ppm. MS (ESI): *m*/*z* (%) = 497 (37) [M$^+$], 415 (100) [M$^+$ – $C_4H_6N_2$].

Imidazolium Salt 7b: 121 mg, 76% yield. $C_{35}H_{34}BF_4FeN_2PS$ (688.36): calcd. C 61.07, H 4.98, N 4.07; found C 60.34, H 4.93, N 3.98. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.67 (s, 1 H, NC*H*N$^+$), 7.84–7.77 (m, 2 H, PPh_2), 7.58–7.28 (m, 9 H, PPh_2 + HC=C Im$^+$), 6.92 (s, 2 H, Mes), 6.71 (s, 1 H, HC=C Im$^+$), 6.66 (d, $J_{H,H}$ = 14.3 Hz, 1 H, CH_2Im$^+$), 5.58 (d, $J_{H,H}$ = 14.3 Hz, 1 H, CH_2Im$^+$), 5.31 (br. s, 1 H, Cp), 4.56 (br. s, 1 H, Cp), 4.35 (s, 5 H, Cp′), 3.96 (br. s, 1 H, Cp), 2.30 (s, 3 H, *p*-CH_3 Mes), 1.84 (br. s, 3 H, *o*-CH_3 Mes), 1.68 (br. s, 3 H, *o*-CH_3 Mes) ppm. $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 141.2 (quat. Mes), 136.2 (NCN$^+$), 135.0 (d, $J_{P,C}$ = 86.0 Hz, quat. PPh_2), 134.2 (quat. Mes), 132.3 (d, $J_{P,C}$ = 87.3 Hz, quat. PPh_2), 132.0 (d, $J_{P,C}$ = 11.0 Hz, 2× PPh_2 + d, $J_{P,C}$ = 3.1 Hz, PPh_2), 131.7 (d, $J_{P,C}$ = 2.9 Hz, PPh_2), 131.4 (d, $J_{P,C}$ = 10.5 Hz, 2× PPh_2), 130.5 (quat. Mes), 129.7 (C-H Mes), 128.6 (d, $J_{P,C}$ = 12.4 Hz, 2× PPh_2), 128.3 (d, $J_{P,C}$ = 12.7 Hz, 2× PPh_2), 122.9 (C=C Im$^+$), 122.2 (C=C Im$^+$), 83.6 (d, $J_{P,C}$ = 12.3 Hz, quat. Cp^C), 76.9 (d, $J_{P,C}$ = 8.6 Hz, Cp), 75.7 (d, $J_{P,C}$ = 11.4 Hz, Cp), 72.9 (d, $J_{P,C}$ = 94.5 Hz, quat. Cp^P), 71.8 (d, $J_{P,C}$ = 10.1 Hz, Cp), 71.4 (Cp′), 48.0 (*C*H_2Im$^+$), 21.0 (*p*-CH_3 Mes), 17.2 (2× *o*-CH_3 Mes) ppm. $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = 40.4 ppm. MS (ESI): *m*/*z* (%) = 601 (100) [M$^+$], 415 (27) [M$^+$ – $C_{12}H_{14}N_2$], 187 (20).

Supporting Information (see footnote on the first page of this article): Full experimental details, ^{1}H, ^{13}C and ^{31}P NMR spectroscopic data, mass spectrometric data and elemental analyses for all new compounds. Crystal data for **4a**, **7a** and **9a** (CCDC-616649 to -616651 contain the supplementary crystallographic data for this paper; these data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif).

Acknowledgments

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