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Bifunctional N-Heterocyclic Carbene Ferrocenyl Ligands - Synthesis and Palladium(II) Complexes

Pauline Loxq,^[a,b] Jean-Claude Daran,^[a,b] Eric Manoury,^[a,b] Rinaldo Poli^[a,b,c] and Agnès Labande^{*[a,b]}

Abstract:

Two ferrocenylimidazolium tetrafluoroborate salts (R = Me, **7** and R = (2,4,6-trimethylphenyl), **8**), precursors of new ferrocenylimidazol-2-ylidene bifunctional ligands, have been prepared for the first time. The free 1-(2-dimethylaminomethyl)ferrocenyl-3-methylimidazol-2-ylidene **12** has been isolated and characterised by ¹H and ¹³C NMR and represents the second example of an isolated and characterised imidazol-2-ylidene directly linked to ferrocene. Neutral (**13**) and cationic (**14**) palladium(II) complexes have been obtained in moderate yields and have been characterised by ¹H and ¹³C NMR and by mass spectrometry.

possesses both planar and central chirality, we chose to design ligands with planar chirality only, similarly to our previous phosphine-functionalized ferrocenyl NHC ligands.^[5]

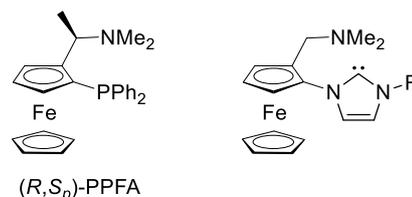


Figure 1. Left: PPFA ligand developed by Hayashi *et al.*^[6]; right: our work.

Introduction

N-heterocyclic carbenes (NHCs) have long been considered as phosphine surrogates, however their rapid development over the past fifteen years has shown that they are much more than that.^[1] There are numerous advantages to work with NHCs, among them the air stability and low toxicity of their precursors (e.g. imidazolium salts) and their usually strong coordination to late transition metals, giving rise to robust, air-stable complexes. The strong σ -donating properties of NHCs combined with their fan-like geometry give them unique reactivity in catalysis, particularly in cross-coupling reactions.^[2,3] However, due to their specific geometry, the synthesis of efficient chiral NHC ligands giving high levels of enantioselectivity in asymmetric catalysis is still a challenge.^[4]

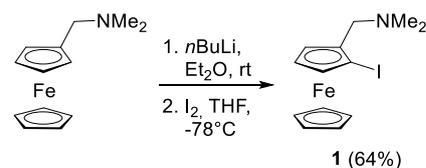
We have recently reported the preparation of planar chiral ferrocenyl phosphine/NHC ligands and their use in the challenging asymmetric version of the palladium-catalysed Suzuki-Miyaura reaction.^[5] These ligands furnished good activities in the cross-coupling reaction of naphthyl bromides with naphthylboronic acid at low catalyst loadings. However, their limited success in terms of enantioselectivity prompted us to design a different family of bifunctional NHC ligands.

Since its synthesis in 1974 by Hayashi *et al.*,^[6] the PPFA ligand has been successfully used in various reactions of asymmetric catalysis (Figure 1).^[7] We describe here a new class of ferrocene-based chiral NHCs based on the PPFA structure, and their coordination to palladium. Whereas the PPFA ligand

Results and Discussion

Synthesis of imidazolium salts

The synthesis of ferrocenyl (benz)imidazolium salts where the heterocycle is directly linked to ferrocene can be carried out by formation of the heterocyclic moiety from aminoferrocene.^[8-10] In our case, further selective introduction in the 2 position of the (dimethylaminomethyl) moiety, if feasible, could have been laborious. It was therefore decided to start the synthesis of the imidazolium salts from commercially available *N,N*-(dimethylaminomethyl)ferrocene. Using a modified procedure from Plenio *et al.*^[11] and Yucel *et al.*^[12], this reagent can easily be functionalised by lithiation in diethyl ether at room temperature followed by reaction of the lithiated species with iodine at -78°C. The 1-iodo-2-(dimethylaminomethyl)ferrocene **1** was obtained in 64% yield as a moderately stable oily solid.



Scheme 1. Synthesis of 1-iodo-2-(dimethylaminomethyl)ferrocene **1**.

The objective was then to introduce the imidazole ring by an Ullman-type coupling reaction. Bolm *et al.* used this strategy to generate compound **A** in 31% yield from iodoferrocene and imidazole with CuI as catalyst in DMSO (Scheme 2).^[13] Later, Nagarkar *et al.* optimised the synthesis using Cu(TMHD)₂ as catalyst and *t*BuOK instead of K₂CO₃ and obtained the product in 46% yield.^[14] Finally, Jiang *et al.* prepared compound **B** in 51% yield, with CuI and 1,2-diaminocyclohexane in the presence of Cs₂CO₃ in dioxane.^[15] This method has the merit of being straightforward but gives the coupling products with poor to moderate yields. We thus studied various reaction parameters in

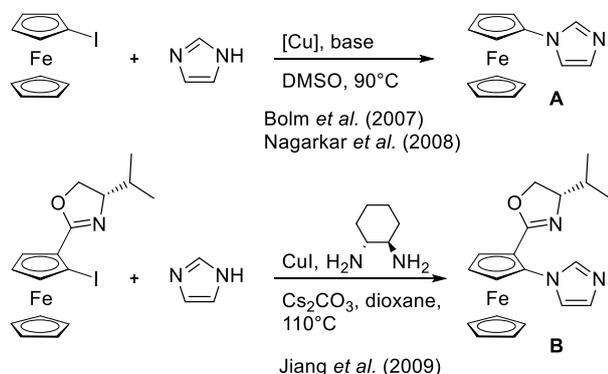
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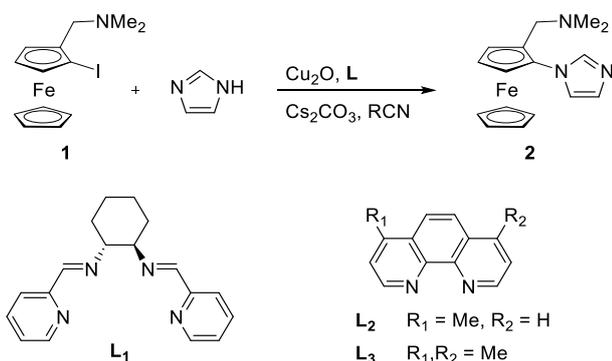
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order to optimise the yield of 1-(imidazol-1-yl)-2-(dimethylaminomethyl)ferrocene, starting from conditions described by Cristau *et al.*^[16] and Cross *et al.*^[17] for the coupling of organic substrates.



Scheme 2. Previous syntheses of imidazol-1-ylferrocene and derivatives by Ullman-type coupling.

1-Iodo-2-(dimethylaminomethyl)ferrocene **1** was reacted with imidazole in the presence of Cu₂O (5 mol%), the tetradentate ligand **L**₁ (20 mol%) and Cs₂CO₃ in refluxing acetonitrile (Scheme 3). After 5 days of heating, the coupling product **2** was obtained in only 30% yield. Buchwald *et al.* reported the use of PEG-3400 as a phase transfer reagent and observed that its addition accelerated the reaction, thanks to its propensity to increase the solubility of carbonates in organic media.^[18a] They also used 4,7-dimethoxy-1,10-phenanthroline instead of ligand **L**₁, in combination with Cu₂O and Cs₂CO₃ in nitrile solvents.^[18b] PEG-3400 was therefore added to the reaction mixture, in the presence of 4-methyl-1,10-phenanthroline (**L**₂), which allowed complete consumption of **1** in 24h instead of 5 days. Several parameters were then changed, such as the nitrile solvent, the temperature, the ligand, the catalytic charge and finally the amount of substrate engaged in the reaction (Table 1).



Scheme 3. Synthesis of **2** via an Ullman-type coupling reaction.

Table 1. Optimisation of reaction parameters for the synthesis of **2**.

Entry	n(1) (mmol)	[Cu] (mol%)	Ligand (mol%)	T (°C)	Solvent	t (h)	Yield (%)
1	2.71	5	L ₁ (20)	80	CH ₃ CN	120	31
2	2.71	5	L ₂ (20)	120	C ₃ H ₇ CN	16	48
3	2.71	5	L ₂ (20)	80	CH ₃ CN	24	48
4	2.71	10	L ₂ (30)	120	C ₃ H ₇ CN	16	27
5	2.71	10	L ₂ (30)	80	CH ₃ CN	24	25
6	2.71	5	L ₃ (20)	120	C ₃ H ₇ CN	16	47
7	8.13	5	L ₂ (20)	120	C ₃ H ₇ CN	16	31

The use of butyronitrile at 120°C allowed the reaction to be complete in 16 h instead of 24 h, however with no yield improvement. Surprisingly, increasing the catalytic charge from 5 mol% to 10 mol% Cu led to lower yields. Finally, the use of more electron-rich 4,7-dimethyl-1,10-phenanthroline (entry 6) did not have any influence on the reaction outcome. The best yield of 1-(imidazol-1-yl)-2-(dimethylaminomethyl)ferrocene **2** (48%, entry 3) was therefore obtained with 5 mol% Cu₂O and 20 mol% 4-methyl-1,10-phenanthroline after 24 h in refluxing acetonitrile. Unfortunately, the yield of **2** dropped to 31% when we tried to scale-up the reaction (entry 7).

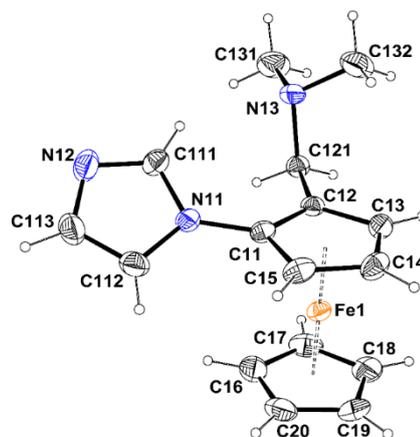


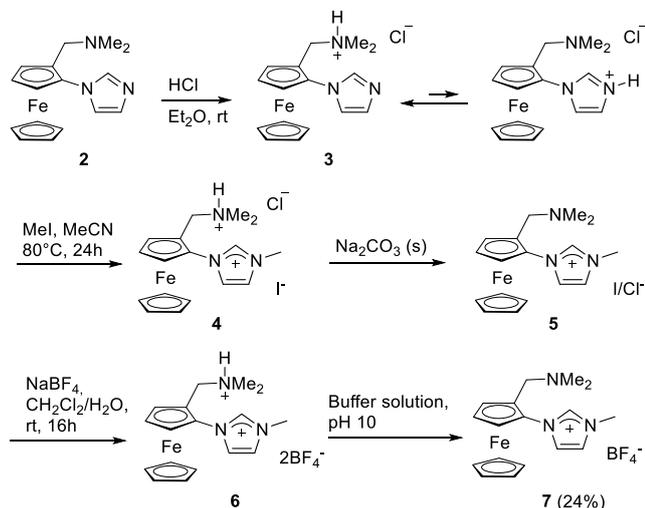
Figure 2. ORTEP representation of 1-(imidazol-1-yl)-2-(dimethylaminomethyl)ferrocene, *rac*-**2**. Ellipsoids are shown at the 50% level. Selected bond lengths (Å) and angles (°): N(11)-C(111), 1.363(3); N(12)-C(111), 1.320(3); C(112)-C(113), 1.360(4); N(11)-C(111)-N(12), 112.1(3).

Compound **2** was fully characterised by usual analytical methods. Its ¹H NMR spectrum shows an AB system at δ ca. 3.3 with a *J*_{HH} coupling constant of 13 Hz, characteristic of diastereotopic methylene protons. X-ray quality orange crystals were obtained by slow evaporation of a concentrated solution of **2** in acetone (Figure 2). The X-ray structure of **2** was compared to

that of (imidazol-1-yl)ferrocene^[19]: bond lengths and angles are similar in both structures and it is interesting to note that the imidazole and cyclopentadienyl rings are not coplanar.

Another interesting feature is the presence of a hydrogen bond between the nitrogen atom of the amino group (N13) and the hydrogen atom on the imidazole C111 atom (calculated value $H(111) \cdots N(13)$: 2.47 Å).

Imidazolium salts were then prepared by reaction of **2** with alkyl halides. Two alkylating agents, i.e. methyl iodide and 2,4,6-trimethylbenzyl bromide, were used so as to introduce substituents generating a different steric bulk. In order to alkylate selectively the imidazole moiety, the more reactive alkylamine had to be protected. The reaction of **2** with one equivalent of $BH_3 \cdot THF$ ^[20] at various temperatures was not efficient since it only led to a mixture of the expected amine-borane complex and of the double adduct, along with some unreacted material. Selective protonation of the amino moiety was thus attempted. Treatment of **2** with one equivalent of HCl in Et_2O afforded a yellow precipitate that was analysed by 1H NMR. The spectrum showed very broad imidazole signals with no shift of the C2 proton to higher frequencies, which leads us to propose the existence of a rapid equilibrium between the expected ammonium form **3** and the imidazolium form (Scheme 4). The pale yellow solid was then taken up into MeCN, an excess of alkylating agent was added and the mixture was heated at reflux during 24h. In the case of MeI, a dicationic compound (**4**), hardly soluble in organic solvents but much more so in water, was obtained. The addition of Na_2CO_3 allowed the deprotonation of **4** to produce the imidazolium salt **5** as an orange solid, soluble in dichloromethane. The formation of the imidazolium salt was confirmed by the presence of a singlet at δ 10.17 in the 1H NMR spectrum, characteristic of the acidic proton situated between the two nitrogen atoms.

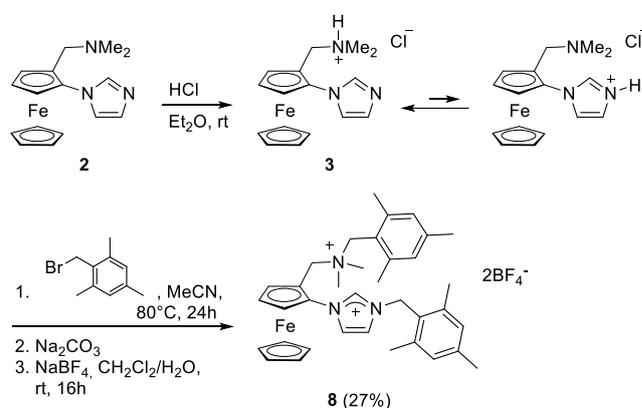


Scheme 4. Synthesis of imidazolium salt **7**.

Compound **5** proved rather unstable, even when stored at $-20^\circ C$ under an inert atmosphere. Therefore, it was submitted to a metathesis reaction to change the iodide/chloride anions with

tetrafluoroborate. A solution of $NaBF_4$ in water was thus added to a dichloromethane solution of **5** and the mixture was vigorously stirred at room temperature for 16h. Under these conditions, the amine is protonated again and the dicationic species **6** is transferred into the aqueous phase. The desired imidazolium salt **7** was regenerated by buffering of the aqueous solution to pH 10 and extraction into dichloromethane.^[21] After work-up, **7** was obtained as a very hygroscopic yellow solid in 24% yield from **2**. The singlet corresponding to the acidic proton of the imidazolium moiety now appears at δ 9.56 in the 1H NMR spectrum, compared to δ 10.17 for **5**, which corroborates the anion exchange. This value is in accord with data found in the literature for analogous compounds.^[22] The low yield of **7** may be partially explained by the existence of an electrostatic repulsion between the two positive charges in intermediates **4** and **6**, which does not favour their formation.

The synthesis of the imidazolium salt bearing a bulkier (2,4,6-trimethylphenyl)methyl substituent was attempted according to a similar procedure. However, the expected imidazolium salt was not obtained. Surprisingly, we observed instead the clean formation of doubly alkylated salt **8** along with some unreacted compound **2**, whereas the expected monoalkylated species was not detected. The introduction of two mesityl substituents makes the ammonium/imidazolium salt rather lipophilic. Hence, contrary to **7**, this compound remains in the organic phase during the metathesis step despite the presence of two positive charges. The ammonium/imidazolium salt **8** was obtained as a yellow solid in 27% yield from **2** (Erreur ! Source du renvoi introuvable.5).



Scheme 5. Synthesis of ammonium/imidazolium salt **8**.

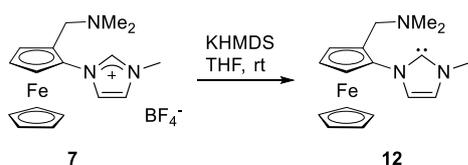
The product was analysed by 1H and ^{13}C NMR: the acidic proton of the imidazolium moiety was found at δ 8.77 in the 1H NMR spectrum. The generation of the doubly alkylated product was confirmed by the presence of two AB systems at δ 5.51-5.46 and 4.40-4.35 integrating for two protons each, in addition to that of the two methylene protons adjacent to ferrocene (at δ 4.76 and 4.61). The two methyl substituents of the amino group appeared in the 1H NMR spectrum as two singlets integrating for 3 protons each, confirming a stable tetrahedral geometry around the nitrogen atom as found in ammoniums. The same behaviour was

observed in the ^{13}C NMR spectrum, with the observation of two signals for the methyl carbon nuclei at δ 47.95 and 47.76. Finally, 18 protons were found between δ 2.31 and 2.29, corresponding to the methyl protons of the mesitylene moieties. This reactivity was only and consistently observed with (2,4,6-trimethylphenyl)methyl bromide, whereas imidazolium salt **7** was the only compound identified in the reaction mixture when methyl iodide was used. The reasons for this unusual reactivity cannot simply be accounted for on grounds of differences in kinetics or pKa values. Therefore, a more thorough experimental study shall be conducted in a future work in order to evaluate the influence of each reaction parameter (i.e. solvent, concentration of reagent), and more particularly the nature of the halogen with the use of (2,4,6-trimethylphenyl)methyl iodide.

Synthesis of palladium complexes

The generation of palladium complexes was first attempted by preparation of intermediate silver complexes. However, the addition of Ag_2O to the imidazolium salt **7** in dichloromethane led to the formation of an intractable black precipitate, probably containing metallic silver.

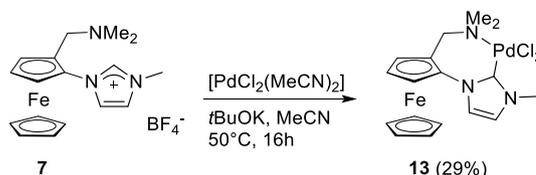
In order to check the feasibility of the reaction, the free carbene was prepared by addition of a solution of potassium bis(trimethylsilyl)amide to a THF solution of imidazolium salt **7** at room temperature (Scheme 6). The initial yellow-orange solution became bright red during the addition of the base. After 20 minutes, the solvent was evaporated in vacuo and the solid analysed by ^1H and ^{13}C NMR in C_6D_6 . The ^1H NMR spectrum showed the disappearance of the imidazolium acidic proton at δ 9.56, giving the first indication for the formation of the free carbene. The ^{13}C NMR spectrum displays a signal at δ 218.56, which corresponds to the carbenic carbon. To our knowledge, this is the second example reported in the literature of an isolated and characterised imidazol-2-ylidene directly linked to ferrocene. The only other example was reported by Togni *et al.* in 2005 and showed a signal at δ 216.10 in the ^{13}C NMR spectrum for the carbenic carbon nucleus.^[9]



Scheme 6. Generation of the free carbene **12**.

The free carbene **12** was then slowly added at room temperature to a THF solution of $[\text{PdCl}_2(\text{MeCN})_2]$. After 16 h at this temperature, a black suspension was observed in a pale yellow solution. Unfortunately, the ^1H NMR revealed that the solution only contained the palladium precursor whereas the ligand decomposed into an intractable black solid. The same reaction conducted at 0°C led to the same result. We finally attempted to generate the palladium complex by in-situ formation of the carbene, in the presence of the palladium salt. Following a procedure reported by Ying *et al.*,^[23] the imidazolium salt **7** was

added to a solution of $[\text{PdCl}_2(\text{MeCN})_2]$ and K_2CO_3 in acetonitrile and the mixture was heated at reflux for 1 h. ^1H NMR analysis of the dark brown residue showed a mixture of starting imidazolium salt **7** and another unidentified ferrocenyl compound. When $t\text{BuOK}$ was used in place of K_2CO_3 and the reaction mixture heated at 50°C for 16 h, the formation of the expected palladium complex **13** was observed (Scheme 7).

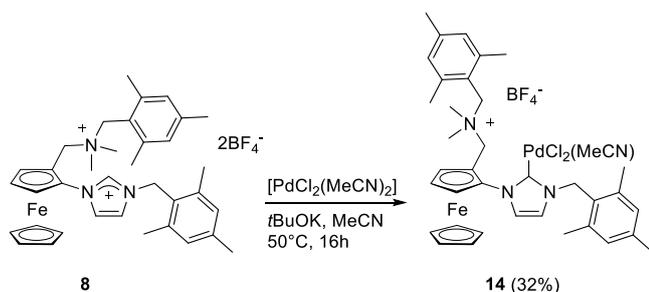


Scheme 7. Synthesis of neutral palladium(II) complex **13**.

First, the ^1H NMR spectrum showed the disappearance of the signal corresponding to the acidic proton of imidazolium. The methyl protons of the amino moiety, visible as one singlet at δ 2.20 integrating for 6 protons in the case of imidazolium salt **7**, appear now as two singlets at δ 2.96 and 2.84, each integrating for 3 protons. The ^{13}C NMR spectrum of **13** clearly indicates the presence of a signal at δ 154.23, typical of carbenic carbon nuclei in Pd(II)-NHC complexes. As a reference, the corresponding signal for a palladium(II) complex bearing a ferrocenyl NHC ligand, reported by Togni *et al.*, appears at δ 151.10.^[9] The palladium complex has also been characterised by high resolution mass spectrometry (ESI): the molecular peak corresponds to complex **13** after the loss of HCl_2^- . This type of rearrangement has already been observed by Douthwaite *et al.* for similar complexes.^[24] The absence of an X-ray structure makes it difficult to confirm the coordination of the amine on the palladium centre. However, in a similar case, Elsevier *et al.* justified the coordination of the amine on palladium by the shift of the ^1H NMR signal of the two methyl groups to higher frequencies.^[25] Their hypothesis has been confirmed by the resolution of the structure by X-ray crystallography. With this data in hand we propose the likely structure of our palladium complex **13** as shown in scheme 8. Air-stable complex **13** has been obtained as a yellow solid in 29% yield.

The same procedure was applied to generate cationic palladium complex **14**, bearing a bulkier CH_2Mes substituent on the NHC moiety, from the ammonium/imidazolium salt **8** (Scheme 8). Complex **14** was obtained as a yellow solid in 32% yield. Similarly to **13**, the ^1H NMR spectrum of this new compound does not show any signal for the acidic proton of imidazolium salt **8**. The two protons of the AB system neighbouring the imidazol-2-ylidene unit split upon coordination of the ligand on palladium and the chemical shift changes from δ 5.51 and 5.46 in **8** to δ 5.86 and 5.52 in **14**. The protons of the AB system situated between the positively charged nitrogen atom and the mesityl moiety also split but do not shift, from δ 4.40 and 4.35 in **8** to δ 4.49 and 4.29 in **14**. Finally, the ^{13}C NMR spectrum shows a signal at δ 149.97 for the carbenic carbon. By comparison with previously reported examples of palladium-NHC complexes,^[26] we propose the

structure represented in Scheme 9. Indeed, the chemical shift observed for the carbenic carbon is typical of a palladium centre bearing one NHC ligand, the coordination sphere being completed by a molecule of acetonitrile. Corresponding ^{13}C NMR chemical shifts for bis-NHC palladium complexes are usually observed at higher frequencies.^[27] Finally, analysis by high resolution mass spectrometry (ESI) gives a peak for $m/z = 546$ corresponding to complex **14** after the loss of HCl_2 , a (2,4,6-trimethylphenyl)methyl fragment and MeCN.



Scheme 8. Synthesis of cationic palladium(II) complex **14**.

Conclusions

The synthesis of two new ferrocenyliimidazolium salts is reported in five steps from commercially available (dimethylaminomethyl)ferrocene. Whereas an amine/imidazolium salt (**7**) was obtained by reaction of protonated 1-(imidazol-1-yl)-2-(dimethylaminomethyl)ferrocene **3** with methyl iodide, the unexpected dialkylated ammonium/imidazolium dicationic species **8** was isolated after reaction of (2,4,6-trimethylphenyl)methyl bromide with intermediate **3**. A free carbene was generated from the imidazolium salt **7**, isolated and characterised by ^1H and ^{13}C NMR. Palladium(II)-NHC complexes were finally prepared by in-situ deprotonation of both imidazolium salts in the presence of a palladium precursor. In the case of complex **13**, amine coordination to the palladium centre is proposed by analogy with existing palladium(II)-NHC/amine complexes. The structure of complex **14**, prepared from the ammonium/imidazolium salt **8**, is believed to be cationic with a monodentate NHC and a dangling ammonium substituent. These new proligands, which present a planar chirality, were prepared as racemic mixtures. The synthesis of enantiopure imidazolium salts and of the corresponding palladium(II) complexes is underway in our laboratories, as well as the evaluation of the latter in catalysis. The results of these investigations will be reported in due course.

Experimental Section

General considerations. All manipulations were performed under an inert atmosphere of dry argon by using vacuum line and Schlenk tube techniques. Solvents for syntheses were dried and degassed by standard methods before use. 1D- and 2D-NMR spectra were recorded on a Bruker

AV400 spectrometer. ^1H and ^{13}C chemical shifts (δ) are given in ppm (the residual peak of deuterated solvent was used as reference). Peaks are labeled as singlet (s), doublet (d), triplet (t), multiplet (m) and broad (br). The proton and carbon assignments were performed by COSY, HSQC, ^1H - ^{13}C HMBC experiments. MS spectra were performed by the mass spectrometry service of the Paul Sabatier University. Commercial chemicals were from Acros, Aldrich, Alfa Aesar, or Fluka and used as received. The buffer solution (pH 10) used for the synthesis of **7** was realised by mixing 100 mL of a 0.05 M aqueous NaHCO_3 solution and 21.4 mL of a 0.1 M aqueous NaOH solution. Abbreviations: Cp_A: cyclopentadienyl ring with $-\text{CH}_2\text{NMe}_2$ and NHC substituents; Cp_B: unsubstituted cyclopentadienyl ring; Fc: ferrocenyl; Im: imidazolyl; Mes: mesityl. C^q: quaternary carbon.

Syntheses

1-iodo-2-(dimethylaminomethyl)ferrocene (1) In a dry Schlenk tube, (dimethylaminomethyl)ferrocene (19.65 g, 80.9 mmol) was dissolved in dry Et_2O (300 mL). *n*-Butyllithium (71 mL, 114 mmol, 1.6M in hexanes) was slowly added at room temperature and the mixture was stirred for 4 h protected from light. After cooling down to -78°C , a solution of I_2 (28.0 g, 110 mmol) in dry THF (75 mL) was added dropwise to the reaction mixture. The temperature was allowed to warm to room temperature over 1 h and stirred at this temperature for 15 min. A 10% aq. $\text{Na}_2\text{S}_2\text{O}_3$ solution (500 mL) was added, the phases were separated and the aqueous phase was extracted with MTBE until the organic extracts were colourless. The organic phases were combined, dried (MgSO_4), filtered and the solvents were evaporated in vacuo. The residue was first purified by column chromatography on basic alumina (eluent: CH_2Cl_2), then on silicagel (eluent: petroleum ether/AcOEt/ NEt_3 : 8/2/1) to afford a red oil that solidifies partly upon standing (19.0 g, 64% yield). ^1H NMR (400 MHz, CDCl_3 , 298 K) δ 4.31 (1H, s br., CH Cp_A), 4.16 (1H, s br., CH Cp_A), 4.08 (1H, t, $J_{\text{HH}} = 2.5$ Hz, CH Cp_A), 3.98 (5H, s, CH Cp_B), 3.24 (2H, s, CH_2), 2.12 (6H, s, CH_3).

1-(imidazol-1-yl)-2-(dimethylaminomethyl)ferrocene (2) Compound **1** (1.0 g, 2.7 mmol), imidazole (220 mg, 3.23 mmol), Cs_2CO_3 (1.7 g, 5.28 mmol), Cu_2O (20 mg, 0.138 mmol), 4-methyl-1,10-phenanthroline (105 mg, 0.54 mmol), PEG-3400 (550 mg) and MeCN (1 mL) were placed in a dry Schlenk tube and heated to 80°C for 24 h. After cooling to room temperature, the black paste was extracted with CH_2Cl_2 until the extracts were colourless. The organic extracts were filtered through Celite® and combined, washed with water and with a 10% aq. $\text{Na}_2\text{S}_2\text{O}_3$ solution, dried (MgSO_4), filtered and evaporated to dryness in vacuo. The residue was purified by column chromatography on silicagel (eluent: petroleum ether/AcOEt: 8/2 with 10% NEt_3). After evaporation of the solvents, the product was dissolved in water and the red solution was extracted with pentane. The organic extracts were combined, washed with water, dried (MgSO_4), filtered and evaporated to dryness in vacuo to afford **2** as an orange crystalline solid (400 mg, 48% yield). ^1H NMR (400 MHz, CDCl_3 , 298K) δ 8.03 (1H, s, N-CH-N), 7.35 (1H, s, CH=CH), 7.09 (1H, s, CH=CH), 4.44 (1H, t, $J_{\text{HH}} = 2$ Hz, CH Cp_A), 4.24 (1H, t, $J_{\text{HH}} = 2.4$ Hz CH Cp_A), 4.20 (5H, s, CH Cp_B), 4.17 (1H, t, $J_{\text{HH}} = 2.4$ Hz, CH Cp_A), 3.46 (1H, AB syst $J_{\text{HH}} = 13$ Hz, CH_2), 3.14 (1H, AB syst $J_{\text{HH}} = 13$ Hz, CH_2), 2.13 (6H, s, 2 CH_3). ^{13}C NMR (100 MHz, CDCl_3 , 298K) δ 139.21 (Im N-CH-N), 128.88 (Im CH=CH), 121.70 (Im CH=CH), 94.61 (C^q Cp_A), 78.80 (C^q Cp_A), 70.23 (Cp_B), 69.18 (CH Cp_A), 64.98 (CH Cp_A), 64.44 (CH Cp_A), 56.46 (CH_2NMe_2), 44.67 (2 CH_3). MS (ESI): m/z 310 [$\text{M}+\text{H}^+$] (75); 265 [$\text{M}-\text{NH}^+\text{Me}_2$] (100). HR-MS (ES+) calcd for $\text{C}_{16}\text{H}_{20}\text{N}_3\text{Fe}$ 310.1881, found 310.1008.

Amine/imidazolium tetrafluoroborate salt (7) In a dry Schlenk tube, HCl (515 μL , 0.515 mmol, 1 mol.L⁻¹ in Et_2O) was slowly added at room temperature to a solution of compound **2** (159 mg, 0.515 mmol) in Et_2O (20 mL). Following the appearance of a yellow precipitate, the mixture was

stirred for 10 min at room temperature. The solvent was evaporated in vacuo and the residue taken up into MeCN (20 mL), then MeI (318 mL, 5.15 mmol) was added with stirring. The mixture was heated at 80°C for 24 h. The solvent was evaporated in vacuo and the residue taken up into CH₂Cl₂. Solid Na₂CO₃ was added and the solution was stirred at room temperature for 20 min, then filtered and concentrated in vacuo. NaBF₄ (10 eq.) and water (10 mL) were added to the CH₂Cl₂ solution and the mixture was vigorously stirred at room temperature for 16 h. The phases were separated, the aqueous phase was buffered to pH 10 and then extracted with CH₂Cl₂. The organic phases were combined, dried (MgSO₄), filtered and concentrated in vacuo. The residue was purified by precipitation by the addition of excess MTBE to a concentrated solution of CH₂Cl₂. The imidazolium salt **7** was obtained as a very hygroscopic yellow solid (50 mg, 24% yield). ¹H NMR (400 MHz, CDCl₃, 298K) δ 9.56 (1H, s, NCHN), 8.04 (1H, pseudo t, J_{HH} = 1.6 Hz, CH=CH), 7.51 (1H, pseudo t, J_{HH} = 1.6 Hz, CH=CH), 4.77 (1H, t, J_{HH} = 2 Hz, CH Cp_A), 4.29 (5H, s, Cp_B), 4.25 (1H, s, CH Cp_A), 4.24 (1H, s, CH Cp_A), 4.06 (3H, s, Im⁺CH₃), 3.73 (1H, AB syst., J_{HH} = 13.2 Hz, CH₂), 2.95 (1H, AB syst., J_{HH} = 13.2 Hz, CH₂), 2.19 (6H, s, N(CH₃)₂). ¹³C{¹H} NMR (100 MHz, CDCl₃, 298K) δ 137.39 (N-CH-N), 124.24 (CH=CH), 123.95 (CH=CH), 92.84 (C^q Cp_A), 78.71 (C^q Cp_A), 71.20 (5 CH Cp_B), 70.43 (CH Cp_A), 65.91 (CH Cp_A), 64.89 (CH Cp_A), 56.40 (CH₂), 44.52 (N(CH₃)₂), 36.78 (Im⁺CH₃). MS (ESI) *m/z* 324 [M⁺] (100). HR-MS (ES⁺) calcd for C₁₇H₂₂N₃Fe 324.1163, found 324.1159.

Ammonium/imidazolium bis(tetrafluoroborate) salt (8) In a dry Schlenk tube, HCl (275 μL, 0.275 mmol, 1 mol.L⁻¹ in Et₂O) was slowly added at room temperature to a solution of compound **2** (85 mg, 0.275 mmol) in Et₂O (10 mL). Following the appearance of a yellow precipitate, the mixture was stirred for 10 min at room temperature. The solvent was evaporated in vacuo and the residue taken up into MeCN (10 mL), then 2,4,6-trimethylbenzyl bromide (293 mg, 1.37 mmol) was added with stirring. The mixture was heated at 80°C for 24 h. The solvent was evaporated in vacuo and the residue taken up into CH₂Cl₂. Solid Na₂CO₃ was added and the solution was stirred at room temperature for 20 min, then filtered and concentrated in vacuo. NaBF₄ (10 eq.) and water (10 mL) were added to the CH₂Cl₂ solution and the mixture was vigorously stirred at room temperature for 16 h. The phases were separated, the organic phase was dried (MgSO₄), filtered and concentrated in vacuo. The residue was purified by precipitation, by addition of excess MTBE to a concentrated solution of CH₂Cl₂. The imidazolium salt **8** was obtained as a very hygroscopic yellow solid (55 mg, 27% yield). ¹H NMR (400 MHz, CD₃CN, 298K) δ 8.78 (1H, s, NCHN), 7.73 (1H, s, CH=CH), 7.20 (1H, s, CH=CH), 7.05 (1H, s, CH Mes), 7.04 (1H, s, CH Mes), 7.02 (2H, s, CH Mes), 5.51 (1H, AB syst. ²J_{HH} = 15 Hz, Im⁺CH₂Mes), 5.46 (1H, AB syst. ²J_{HH} = 15 Hz, Im⁺CH₂Mes), 5.00 (1H, s, CH Cp_A), 4.87 (1H, s, CH Cp_A), 4.76 (1H, AB syst. ²J_{HH} = 14 Hz, FcCH₂N⁺), 4.75 (1H, s, CH Cp_A), 4.61 (1H, AB syst. ²J_{HH} = 14 Hz, FcCH₂N⁺), 4.56 (5H, s, CH Cp_B), 4.40 (1H, AB syst., ²J_{HH} = 14 Hz, N⁺CH₂Mes), 4.35 (1H, AB syst., ²J_{HH} = 14 Hz, N⁺CH₂Mes), 2.64 (3H, s, N⁺CH₃), 2.44 (3H, s, N⁺CH₃), 2.31 (9H, m, CH₃Mes), 2.29 (9H, s, CH₃Mes). ¹³C NMR (100 MHz, CD₃CN, 298K) δ 140.73 (2 C^q Mes), 140.64 (C^q Mes), 140.06 (C^q Mes), 138.58 (2 C^q Mes), 137.57 (NCHN), 130.52 (2 CH Mes), 129.72 (2 CH Mes), 126.00 (CH=CH), 125.41 (C^q Mes), 122.65 (CH=CH), 121.51 (C^q Mes), 94.80 (C^q Cp_A), 73.01 (CH Cp_A), 72.01 (5 CH Cp_B), 70.09 (CH Cp_A), 69.41 (CH Cp_A), 67.83 (C^q Cp_A), 62.83 (FcCH₂N⁺), 61.47 (N⁺CH₂Mes), 48.12 (Im⁺CH₂Mes), 47.95 (CH₃N⁺), 47.76 (CH₃N⁺), 20.57 (2 CH₃Mes), 20.14 (CH₃Mes), 20.02 (CH₃Mes), 18.88 (2 CH₃Mes). MS (ESI) *m/z* 442 [M²⁺ - (C₁₀H₁₃)⁺] (100), 397 [M²⁺ - (NHMe₂C₁₀H₁₃)⁺] (28), 133 [C₁₀H₁₃]⁺ (30). HR-MS (ES⁺) calcd for C₂₆H₃₂N₃Fe 442.1992, found 442.1984.

Amine/N-heterocyclic carbene (12) In a dry Schlenk tube, imidazolium salt **7** (71 mg, 0.173 mmol) was dissolved in dry THF (4.3 mL). KHMDS (360 μL, 0.181 mmol, 0.5 mol.L⁻¹ in toluene) was added dropwise at room temperature and the solution was stirred for 20 min. The solvents were

evaporated in vacuo to afford carbene **12** as a bright red solid. ¹H NMR (400 MHz, C₆D₆, 298 K) δ 7.66 (1H, s, CH=CH), 6.42 (1H, s, CH=CH), 4.90 (1H, s, CH Cp_A), 4.30 (5H, s, CH Cp_B), 4.04 (1H, d, J_{HH} = 12 Hz, CH₂), 3.99 (1H, s, CH Cp_A), 3.94 (1H, s, CH Cp_A), 3.52 (3H, s, ImCH₃), 3.16 (1H, d, J_{HH} = 12 Hz, CH₂), 2.22 (6H, s, N(CH₃)₂). ¹³C{¹H} NMR (100 MHz, C₆D₆, 298 K) δ 218.56 (C^q, N-C-N), 122.24 (CH, CH=CH), 118.61 (CH, CH=CH), 100.99 (C^q, Cp_A), 78.18 (C^q, Cp_A), 70.77 (5 CH Cp_B), 68.50 (CH Cp_A), 65.69 (CH Cp_A), 64.22 (CH, Cp_A), 57.07 (CH₂), 44.77 (N(CH₃)₂), 29.97 (ImCH₃).

Palladium complex (13) In a dry Schlenk tube, the imidazolium salt **7** (26 mg, 0.063 mmol) and [PdCl₂(MeCN)₂] (17 mg, 0.066 mmol) were dissolved in dry MeCN (30 mL). *t*BuOK (10 mg, 0.089 mmol) was added and the mixture was heated at 50°C for 16h. The solvent was evaporated in vacuo, the residue taken up into acetone and the solution was filtered through Celite®. After removal of the solvent, the residue was purified by precipitation, by addition of excess MTBE to a concentrated solution of CH₂Cl₂. The palladium complex **13** was obtained as a yellow solid (10 mg, 32% yield). ¹H NMR (400 MHz, CDCl₃, 298 K) δ 7.46 (1H, d, J_{HH} = 2 Hz, CH=CH), 7.11 (1H, d, J_{HH} = 2 Hz, CH=CH), 4.78 (1H, s, CH Cp_A), 4.44 (1H, s, CH Cp_A), 4.37 (1H, t, J_{HH} = 2 Hz, CH Cp_A), 4.21 (5H, s, CH Cp_B), 4.19 (3H, s, Im-CH₃), 3.32 (1H, AB syst., J_{HH} = 13 Hz, CH₂), 3.23 (1H, AB syst., J_{HH} = 13 Hz, CH₂), 2.96 (3H, s, N-CH₃), 2.84 (3H, s, N-CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃, 298 K) δ 154.23 (C^q, C-Pd), 123.90 (CH, CH=CH), 123.86 (CH, CH=CH), 97.53 (C^q Cp_A), 77.80 (C^q Cp_A), 70.44 (5 CH Cp_B), 69.05 (CH Cp_A), 66.27 (CH Cp_A), 66.20 (CH₂), 63.19 (CH Cp_A), 53.39 (N-CH₃), 51.53 (N-CH₃), 39.12 (Im-CH₃). MS (ESI) *m/z* 428 [M-HCl₂]⁺ (100). HR-MS (ES⁺) calcd for C₁₇H₂₀N₃FePd 428.0051, found 428.0054.

Palladium complex (14) In a dry Schlenk tube, the imidazolium salt **8** (24 mg, 0.032 mmol) and [PdCl₂(MeCN)₂] (12.3 mg, 0.047 mmol) were dissolved in dry MeCN (30 mL). *t*BuOK (8 mg, 0.071 mmol) was added and the mixture was heated at 50°C for 16 h. The solvent was evaporated in vacuo, the residue taken up into acetone and the solution was filtered through Celite®. After removal of the solvent, the residue was purified by precipitation, by addition of excess MTBE to a concentrated solution of acetone. Complex **14** was obtained as a yellow solid (10 mg, 32% yield). ¹H NMR (400MHz, CD₃CN, 298K) δ 7.49 (1H, d, ³J_{HH}=2 Hz, CH=CH), 7.06 (2H, s, CH Mes), 7.03 (2H, s, br., CH Mes), 6.39 (1H, d, ³J_{HH}=2 Hz, CH=CH), 6.28 (1H, s, br., CH Cp_A), 5.86 (1H, AB syst. ²J_{HH}=14 Hz, ImCH₂Mes), 5.52 (1H, AB syst. ²J_{HH}=14 Hz, ImCH₂Mes) 4.08 (2H, s, br., CH Cp_A), 4.64 (1H, AB syst. ²J_{HH}=14 Hz, FcCH₂N⁺), 4.61 (1H, AB syst. ²J_{HH}=14 Hz, FcCH₂N⁺), 4.49 (1H, AB syst. ²J_{HH}=14 Hz, N⁺CH₂Mes), 4.44 (5H, s, CH Cp_B), 4.29 (1H, AB syst. ²J_{HH}=14 Hz, N⁺CH₂Mes), 2.72 (3H, s, N⁺CH₃), 2.44 (3H, s, N⁺CH₃), 2.37 (3H, s, CH₃ Mes), 2.36 (3H, s, CH₃ Mes), 2.25 (3H, s, CH₃ Mes), 2.23-2.19 (9H, m, CH₃ Mes). ¹³C{¹H} NMR (100MHz, CD₃CN, 298K) δ 149.97 (C^q C-Pd), 141.56 (2 C^q Mes), 141.46 (C^q Mes), 140.37 (C^q Mes), 139.67 (2 C^q Mes), 131.59 (CH Mes), 131.47 (CH Mes), 130.45 (CH Mes), 130.41 (CH Mes), 127.95 (C^q Mes), 125.58 (Im CH=CH), 122.91 (C^q Mes), 121.81 (Im CH=CH), 99.21 (C^q Cp_A), 73.25 (CH Cp_A), 72.45 (5CH Cp_B), 72.37 (CH Cp_A), 69.21 (CH Cp_A), 67.38 (C^q Cp_A), 63.48 (FcCH₂N⁺), 63.01 (N⁺CH₂Mes), 50.45 (ImCH₂Mes), 49.75 (CH₃N⁺), 49.16 (CH₃N⁺), 21.81 (2 *o*-CH₃ Mes), 21.22 (*p*-CH₃ Mes), 20.96 (*p*-CH₃ Mes), 20.20 (2 *o*-CH₃ Mes). MS (ESI) *m/z* 546 [M⁺ - (C₁₀H₁₃)(CH₃CN)HCl₂] (60), 133 [C₁₀H₁₃]⁺ (100). HR-MS (ES⁺) calcd for C₂₆H₃₀N₃FePd 546.0836, found 546.0837.

X-ray structural analyses. A single crystal of compound **2** was mounted under inert perfluoropolyether in a loop at the tip of a fiber and cooled in the cryostream of an Agilent Technologies GEMINI EOS CCD diffractometer. The structure was solved by direct methods (SIR97^[28]) and refined by least-squares procedures on *F*² using SHELXL-97^[29]. The crystal is twinned by reticular merohedry. The twin results from a 180.0 degree rotation about 1. 0. 0. direct lattice direction:

[1.000 0.000 0.000]
 [-0.487 -1.000 0.000]
 [0.000 0.000 -1.000]

The two domains are in the ratio 1/4. All H atoms attached to carbon were introduced in calculation at idealized positions and treated as riding models. The drawing of the molecules was realized with the help of ORTEP32 [30].

Table 2. Crystal data and structure refinement for compound **2**.

Identification code	2	
Empirical formula	C32 H38 Fe2 N6	
Formula weight	618.38	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.7001(4) Å	$\alpha = 82.391(2)^\circ$
	b = 11.7339(4) Å	$\beta = 89.823(2)^\circ$
	c = 11.8988(3) Å	$\gamma = 102.838(3)^\circ$
Volume	1442.95(8) Å ³	
Z	2	
Density (calculated)	1.423 Mg/m ³	
Absorption coefficient	1.038 mm ⁻¹	
F(000)	648	
Crystal size	0.3 x 0.22 x 0.18 mm ³	
Theta range for data collection	3.013 to 27.103°.	
Reflections collected	32998	
Independent reflections	32998	
Completeness to theta = 27.100°	99.8 %	
Refinement method	F ²	
Data / restraints / parameters	32998 / 0 / 366	
Goodness-of-fit on F ²	1.030	
Final R indices [I > 2sigma(I)]	R1 = 0.0370, wR2 = 0.0811	
R indices (all data)	R1 = 0.0492, wR2 = 0.0893	
Largest diff. peak and hole	0.549 and -0.404 e.Å ⁻³	

CCDC-1028945 for compound **2** contains 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/data_request/cif.

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Keywords: Carbene ligands • Ferrocenes • N ligands • Palladium

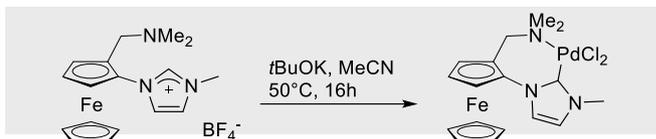
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**New Bifunctional N-Heterocyclic
Carbene Ferrocenyl Ligands:
Synthesis and Palladium(II)
Complexes**

Two ferrocenyl imidazolium tetrafluoroborate salts (R = Me and (2,4,6-trimethylphenyl)), precursors of new ferrocenyl imidazol-2-ylidene bifunctional ligands, and the corresponding palladium(II) complexes have been prepared for the first time.
