N-Ferrocenyl-Substituted Planar-Chiral N-Heterocyclic Carbenes and Their Pd^{II} Complexes

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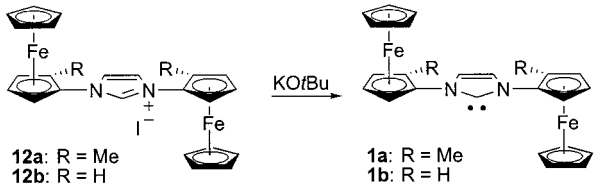
The *N*-ferrocenyl-linked N-heterocyclic carbenes **1a** and **1b** were obtained by treatment of their imidazolium salts **12a** and **12b** with potassium *tert*-butoxide. The latter were shown to be accessible from (*R*)-1-amino-2-methylferrocene (**9**) and aminoferrocene, respectively, which were converted into the corresponding formamidines and then subjected to a novel cyclization procedure. Treating the ligand precursors **12a** and **12b** with $[Pd(OAc)_2]_3$ under different reaction conditions afforded the *trans*-pyridine-substituted Pd^{II} complexes **14a** and **14b** as well as their *trans*-triphenylphosphane-substituted counterparts **16a** and **16b** and, in the case of the chiral ligand precursor, the dinuclear Pd^{II} complex **15a**. Conformational analysis of the ligands based on the X-ray structures of **12a**, **12b** and **16a** revealed the dependence of the two torsion angles between the central imidazolium core and the adjacent ferrocenyl substituents on the steric and electronic properties of the observed systems.

Introduction

Phosphanes bearing planar-chiral ferrocenyl groups are established ligands in coordination chemistry and have proven to be very successful in asymmetric catalysis.[1] Although N-heterocyclic carbenes (NHCs) may often act as phosphane substitutes, leading to considerably improved performances of the resultant catalysts,[2−5] both achiral and chiral ferrocenyl-substituted NHCs are still rare.[6−16] These can be divided into two classes: either directly *N*-ferrocenyl-substituted[6,7] or linked by a methylene, ethylene[10,11,16] or an ethenyl spacer.[12−15] The latter are of particular interest as bi- or tridentate ligands,[13,15] while for monodentate ligands it seems appropriate to further restrict the conformational freedom to the rotation around the two nitrogen−ferrocenyl bonds, thus leading to directly *N*-ferrocenyl-substituted carbenes.[17] Achiral *N*,*N*′-diferrocenyl-substituted imidazolium salts[18] are known in the literature but the reported yields of their synthesis are moderate and the salts resisted controlled deprotonation.[6]

Square-planar Pd^{II} complexes serve as catalyst precursors in numerous cross-coupling and Heck-type reactions. Recently, chiral monodentate NHCs have been shown to be the ligands of choice in Pd-catalyzed asymmetric α-arylations of carbonyl compounds, of which cyclic amide α-arylations gave the best results.[19] Pd complexes bearing chiral monodentate NHCs are still rare and complexes bearing planar-chiral monodentate NHCs are as-yet unknown. We reasoned that ligands showing the steric features of **1a** and **1b** attached to Pd^{II}, in combination with two halides and one potentially labile ligand, might lead to active systems for the above-mentioned asymmetric catalytic applications. We report here a new, high-yielding synthetic strategy leading to the isolation of both achiral and chiral imidazolium iodides **12a** and **12b** that can be deprotonated to the carbenes **1a** and **1b** (Scheme 1). Complexes showing the desired constitution were synthesized from $[Pd(OAc)_2]_3$ and proved to be active catalyst precursors in amide α-arylations.



Scheme 1

Results and Discussion

Ligand Synthesis

The chiral imidazolium iodide **12a** was synthesized from the known chiral acetal **2**[20] in ten steps in an overall yield of 30% (Scheme 2). Thus, stereoselective lithiation of **2** followed by electrophilic quenching with methyl iodide led to the planar-chiral acetal **3**, which was then converted into the aldehyde **4**. The carboxylic acid **6a**, which served as starting material in the following reaction sequence, was

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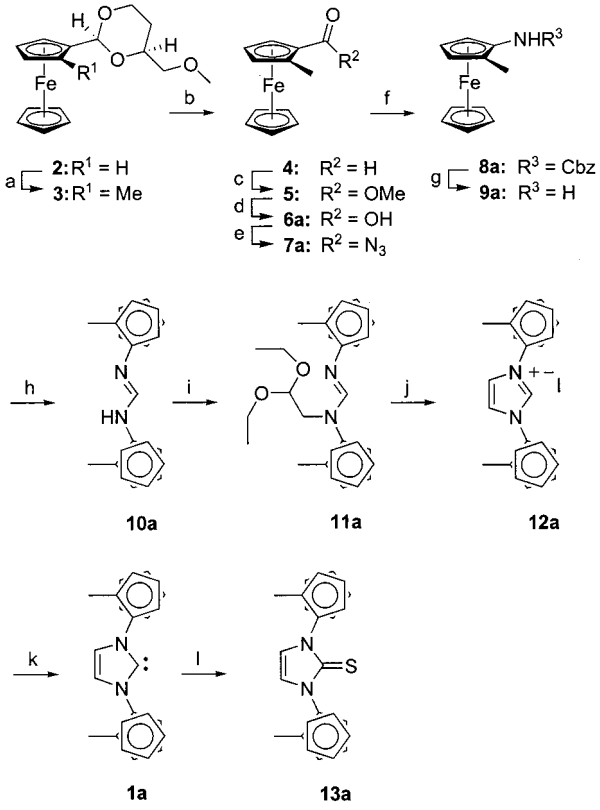
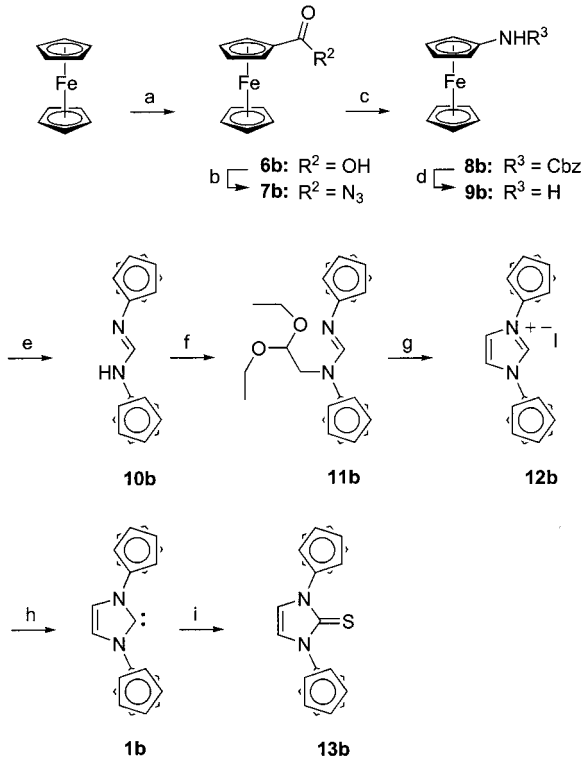
produced by iodine-mediated oxidation of the aldehyde **4**[21] to the ester **5**, followed by saponification. Its achiral counterpart **6b** is accessible by carboxylation of monolithioferrocene generated in situ from ferrocene (Scheme 3).[22]



Scheme 2. Conditions: (a) *t*BuLi, Et_2O, −78 °C to room temp. then MeI, Et_2O, −78 °C, 95%; (b) PTSA monohydrate, H_2O, CH_2Cl_2, room temp., 98%; (c) I_2, KOH, MeOH, 0 °C to room temp. 77%; (d) NaOH, EtOH, H_2O, room temp., 93%; (e) i) preparation of activating reagent (in situ): DMF, thionyl chloride, benzene, room temp.; ii) reaction: activating reagent, NaN_3, py, Bu_4NBr, CH_2Cl_2, room temp., in situ; (f) benzylic alcohol, 90 °C, 81% (two steps); (g) H_2, Pd/C, Me_2CHOH, room temp., quant.; (h) *s*-triazine, dioxane, 100 °C, quant.; (i) bromoacetaldehyde diethylacetal, NaH, DMF, 75 °C, 82%; (j) $BF_3{\cdot}OEt_2$, NaI, MeCN, room temp., 71%; (k) KO*t*Bu, pentane, room temp.; (l) S_8, benzene, room temp.



Scheme 3. Conditions: (a) *t*BuLi, THF, −78 °C to room temp. 67%; (b) i) preparation of activating reagent (in situ): DMF, thionyl chloride, benzene, room temp.; ii) reaction: activating reagent, NaN_3, py, Bu_4NBr, CH_2Cl_2, room temp., in situ; (c) benzylic alcohol, 90 °C, 55% (two steps); (d) H_2, Pd/C, Me_2CHOH, room temp., 96%; (e) *s*-triazine, dioxane, 100 °C, 96%.; (f) 2-bromo-1,1-diethoxyethane, NaH, DMF, 75 °C, 79%; (g) $BF_3{\cdot}OEt_2$, NaI, MeCN, room temp., 75%; (h) KO*t*Bu, pentane, room temp.; (i) S_8, benzene, room temp.

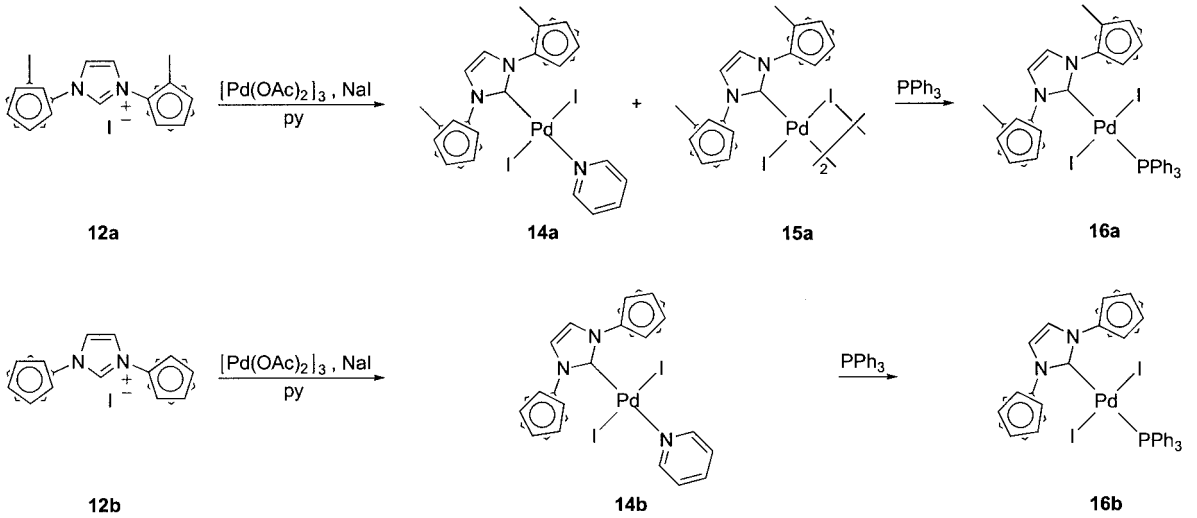
Apart from the cyclization procedure discussed below, another major challenge in the present ligand synthesis was the generation of the nitrogen-ferrocene bond. Since aminoferrocenes serve as intermediates in the synthesis of various ligands and optically active materials, this problem has attracted considerable interest.[23−28] One of the oldest routes[26] is based on a Curtius degradation of ferrocenecarboxylic acid chloride; other methods have used bromoferrocene[29−31] or ferroceneboronic acid[32] as starting material for copper-mediated amination reactions. Based on its simplicity and on the easy accessibility of its starting materials, we chose to use the Curtius rearrangement sequence, which, in our case, proved to be attractive both in terms of synthetic feasibility and the high isolated yields of the products. The chiral acid **6a** as well as the achiral acid **6b** were activated[33] and converted, in situ, into the ferrocenyl carbonyl azides **7a** and **7b**, which rearranged upon heating to the corresponding isocyanates. Addition of benzylic alcohol followed by heating generated the carbamic acid esters **8a**,**b** in a one-pot procedure from **6a**,**b** (Scheme 2 and 3). Reductive deprotection of the Cbz-protected amines **8a**,**b** led to the electron rich, strongly nucleophilic and air-sensitive amines **9a**,**b**.[34]

The most frequently used reaction sequence from primary amines to imidazolium salts involves condensation of the amines with a 1,2-dialdehyde to yield the corresponding diimine. Conversion of the latter with a one-carbon synthetic equivalent in the formal oxidation state of formaldehyde then leads to an imidazolium salt that is suitable for deprotonation. In contrast to a recently published procedure,[6] we decided not to construct the heterocyclic core of the target molecule by condensation of the ferrocenylamines with glyoxal, followed by cyclization with formaldehyde, due to low reported yields and demanding purifications. Instead, we chose to transform the ferrocenylamines **9a** and **9b** into *N*,*N*′-diferrocenyl-substituted amidines and to use the latter as intermediates in the cyclization sequence. The amidines **10a**,**b** were easily obtained from the amines **9a**,**b** by methinyl group transfer from *s*-triazine[35] and could be considered as being interesting potential ligands in their own right. The missing C_2 fragment was in-

corporated into the structures by treating the amidinate anions of **10a**,**b** with 2-bromo-1,1-diethoxyethane to give the acetals **11a**,**b**.[36] Addition of an excess of $BF_3{\cdot}OEt_2$ led to the desired cyclization and to the 4-ethoxy-4,5-dihydroimidazolium cation, which, under prolonged heating, eliminated ethanol to form the aromatic target core. The imidazolium iodides **12a**,**b** were obtained after anion exchange and column chromatography. It is noteworthy that in the high yielding reaction sequence from the carbamic acid esters **8a**,**b** to the imidazolium iodides **12a**,**b** only one chromatographic purification of the products and intermediates is required. Both chiral and achiral carbenes **1a** and **1b** were prepared by adding potassium *tert*-butoxide to a slurry of the imidazolium iodides **12a** or **12b** in pentane, followed by evaporation of the solvent and selective extraction of the products with benzene. The carbenes proved to be stable in solution in C_6D_6 over a period of 24 hours without any sign of decomposition, as ascertained by ^{1}H NMR spectroscopy. In the ^{13}C NMR spectra the diagnostic chemical shifts at δ = 221.1 ppm (**1a**) and 216.1 ppm (**1b**) were detected. Adding S_8 to either of the carbenes resulted in the formation of the corresponding thiones **13a** and **13b** (Scheme 2 and 3).

Synthesis of Palladium Complexes

A series of NHC-substituted Pd^{II} complexes were obtained from the reaction of the imidazolium iodides **12a**,**b** with $[Pd(OAc)_2]_3$ under different reaction conditions (Scheme 4). We reasoned that Pd complexes substituted with one NHC, two halides and one hemilabile ligand might be potent precatalysts for both Heck-type and cross-coupling reactions since, in both cases, at least one ligand stabilizing the active Pd^0 species as well as two free coordination sites *cis* to each other are required in the catalytic cycle. While the bulky and strongly bound carbene ligand is supposed to stabilize the active Pd^0 species and prevent precipitation of Pd black, the hemilabile ligand can be split off previous to oxidative addition of the aryl halide substrate. Pyridine seemed to be an advantageous hemilabile ligand as it can also be used in large excess as a solvent in the preparation of the catalyst precursor. Further advantage can be taken of its high dielectric constant, which allows complete dissolution of the imidazolium iodides, and of its ability to act as a base, which might facilitate the in situ deprotonation of the imidazolium iodides. Thus, reaction of **12b** and $[Pd(OAc)_2]_3$ in the presence of sodium iodide in pyridine afforded the pyridine-substituted complex **14b** regardless of whether one or two equivalents of the imidazolium iodide were used. Small amounts of the known complex $PdI_2(pyridine)_2$ were separated from the main product by column chromatography. Subjecting the chiral imidazolium iodide **12a** to the same reaction conditions resulted in an isolated equimolar mixture of both the pyridine-substituted complex **14a** and the equivalent iodo-bridged dinuclear derivative **15a**. Interestingly, the ^{1}H NMR spectrum of the chromatographed mixture showed that the iodo-bridged dimer **15a** contains two non-equivalent ferrocenyl ligands, thereby indicating restricted rotation around the Pd−C bond. This phenomenon has been observed before in an analogous bridged complex bearing two ethenyl-linked, diferrocenyl-substituted chiral NHCs that have been characterized by NMR spectroscopy and X-ray diffraction studies.[37] In analogy to that case it seems very likely that the observed anisotropy of the ferrocenyl substituents results from the typical butterfly conformation of the Pd_2I_2 core.[38] Upon adding triphenylphosphane, the mixture of the two chiral complexes **14a** and **15a** was cleanly converted into the carbene phosphane complex **16a**, whose *trans* configuration was determined by X-ray analysis (vide infra). The achiral, pyridine-substituted complex **14b**, under the same reaction conditions, gave the analogous complex **16b**. The *trans* configuration of both complexes **16a** and **16b** was further supported by the large coupling constants between the phosphorus nuclei and the carbene carbon nuclei.[39] Long-range coupling to the olefinic carbons of the NHC over four bonds and long-range coupling to the olefinic hy-



Scheme 4

drogen atoms over five bonds were observed.[39] Selective saturation of the phosphorus hydrogen transition resulted in a decoupled ^{1}H NMR spectrum, as performed in the case of **16a**.

Crystal Structures and Conformational Analysis

Single-crystal X-ray analysis of the imidazolium iodides **12a** (Figure 1) and **12b** (Figure 2) showed the expected bond lengths and angles within the imidazolium cores, thus indicating that the steric and electronic features of the ferrocenyl subunits do not significantly alter the properties of the heterocycle. In both cations the ferrocenyl−imidazolium bond lengths lie in the range of a C−N single bond, thus excluding delocalisation of the π electrons between the cyclic moieties of the molecules. This conclusion is in agreement with the observed non-planar arrangement of the three connected cyclic subunits.[40] The ferrocenyl−methyl bond lengths in **12a** do not show any deviation from the expected value.

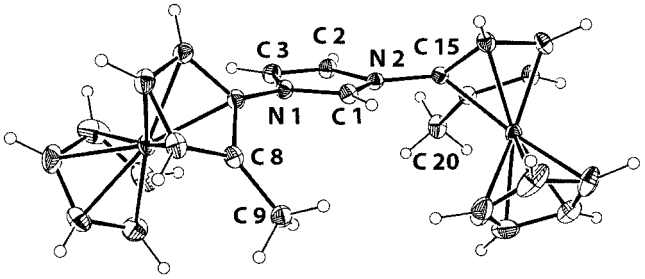


Figure 1. ORTEP view of the cation of **12a**, with 30% thermal ellipsoids; selected bond lengths [A] and angles [°]: C(1)−N(1) 1.327(3), C(1)−N(2) 1.332(3), C(2)−C(3) 1.346(4), N(1)−C(3) 1.378(3), N(2)−C(2) 1.387(3), N(1)−C(4) 1.426(3), N(2)−C(15) 1.420(3), C(8)−C(9) 1.498(4), C(19)−C(20) 1.492(3); N(1)−C(1)−N(2) 108.6(2), C(1)−N(1)−C(4)−C(8) 310.5(4), C(1)−N(2)−C(15)−C(19) 143.8(3)

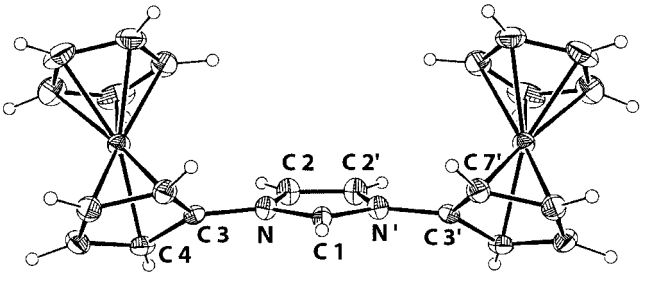


Figure 2. ORTEP view of the cation of **12b**, with 30% thermal ellipsoids; selected bond lengths [A] and angles [°]: C(1)−N(1) 1.329(8), C(2)−C(2′) 1.331(14), N−C(2) 1.380(8), N−C(3) 1.419(8); N−C(1)−N′ 108.4(8), C(1)−N−C(3)−C(4) 139.4(8), C(1)−N′−C(3′)−C(7′) 320.9(11)

X-ray analysis of the chiral Pd complex **16a** (Figure 3) reveals that the main structural features of **12a**, apart from the torsion angles, are preserved in the ligand. While the extent of delocalization in the heterocyclic fragment is slightly decreased and the N−C−N angle is reduced from 108.6(2)° to 104.9(3)°, the ferrocenyl−imidazolium bond lengths stay constant. The palladium−carbon bond of 2.004(3) Å lies in the typical range.[40]

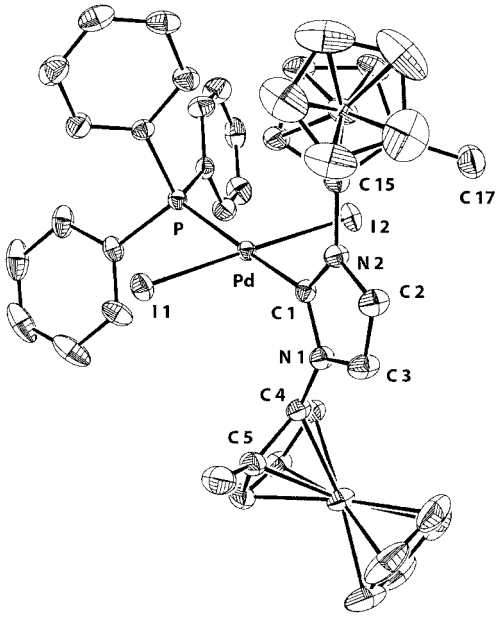


Figure 3. ORTEP view of the complex **16a**, with 30% thermal ellipsoids; hydrogen atoms are omitted for clarity; selected bond lengths [A] and angles [°]: C(1)−Pd 2.004(3), Pd−P 2.3298(9), Pd−I(1) 2.6280(5), Pd−I(2) 2.5932(5), C(1)−N(1) 1.351(4), C(1)−N(2) 1.359(4), C(2)−C(3) 1.323(5), N(1)−C(3) 1.385(4), N(2)−C(2) 1.386(5), N(1)−C(4) 1.426(4), N(2)−C(15) 1.430(4), C(5)−C(6) 1.489(6), C(16)−C(17) 1.502(6); N(1)−C(1)−N(2) 104.9(3), C(1)−N(1)−C(4)−C(5) 246.0(4), C(1)−N(2)−C(15)−C(16) 245.4(4)

Since the overall shape of the ligand and, as a consequence, its ability to efficiently transfer chirality in asymmetric catalytic reactions depends on its conformation, it is important to note that the latter is fully described by the two torsion angles between the central imidazolium core and the adjacent ferrocenyl substituents. Rotation around the two ferrocenyl−nitrogen bonds in solution at room temperature proved to be fast on the NMR timescale for **12b**, **13b**, **14b** and **16b**. No such conclusions can be drawn for their chiral counterparts due to symmetry restrictions. In the crystal structures, however, well-defined conformations could be studied. In **12a** torsion angles of 310.5(4)° and 143.8(3)° around C(1)−N(1)−C(4)−C(8) and C(1)−N(2)−C(15)−C(19), respectively, were detected. The corresponding angles in **12b** around C(1)−N−C(3)−C(4) and around C(1)−N′−C(3′)−C(7′) are 139.4(8)° and 320.9(11)°, respectively, whereas the C(1)−N(1)−C(4)−C(5) and C(1)−N(2)−C(15)−C(16) angles in **16a** are 246.0(4)° and 245.4(4)°, respectively. These at-first-sight arbitrary results can be rationalized by uncovering the forces that determine the torsion angles.

Conformational analysis of the solid-state structures of compounds **12a**, **12b**, **16a** and of two analogous achiral derivatives reported by Bildstein et al.[6] reveals that their conformations are mainly governed by two opposing forces: i) pseudo allylic repulsion[41] between the *ortho* substituents of the ferrocenyl fragments and the *ortho* substituents of the heterocycle, and ii) steric interactions between the substituents on the imidazolium core and the unsubstituted Cp

ring. The orientation of the two ferrocenyl planes with respect to each other appears to be of minor importance, as can be seen by comparing the orientations in the crystal structures of, for example, **12a** and **12b**. Therefore, the two torsion angles in a molecule can be analyzed separately, thus simplifying the analysis: only the tilt angles ($0° \leq$ tilt angle $\leq 90°$) between the ferrocenyl planes and the heterocyclic plane need to be considered as relevant. As shown in Figure 4, all known tilt angles of the discussed imidazolium salts lie in a specific range between 36.2(3)° and 49.5(4)°, whereas the sulfur adduct **13b**[6] shows slightly larger angles of 53.7(3)°. This shows that even small atoms or substituents such as hydrogen, methyl or thiooxo attached to the position adjacent to the bond connecting the Cp and the heterocycle on either of the cyclic moieties exclude tilt angles near to 0° or 90°. The rotational potential energy changes around the energy minima seem to be small. Only in **16a**, where two substituents *ortho* to the flexible bond are present, is it not surprising to find considerably increased torsion angles of 65.4(4)° and 66.0(4)° (Figure 4).

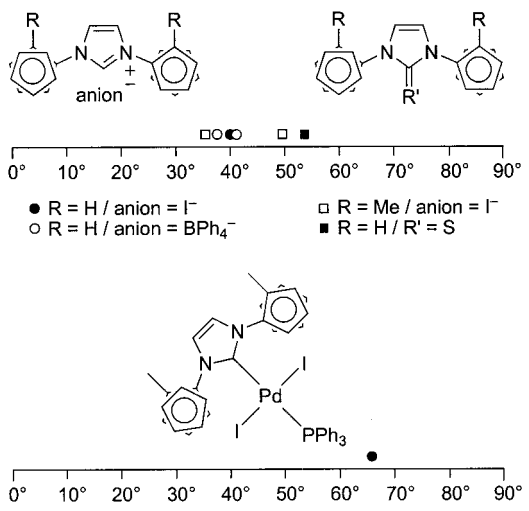


Figure 4. Tilt angles between planes of the Cp substituent and the heterocyclic core in imidazolium cations, in a thione and in a Pd-bound carbene ligand

Conclusion

The bulky, planar-chiral, *N*-ferrocenyl-substituted NHC **1a** as well as its achiral analog **1b** were synthesized by deprotonation of their imidazolium iodide precursors **12a** and **12b**. The latter were prepared by a synthetic strategy based on a Curtius degradation to form the ferrocenyl−nitrogen bond and a novel cyclization procedure to build up the heterocyclic cores of the target molecules. The reaction of **12b** with $[Pd(OAc)_2]_3$ in the presence of pyridine led to the *trans*-pyridine-substituted complex **14b**, but when **12a** was subjected to the same reaction conditions a mixture of the mononuclear complex **14a** and the dinuclear complex **15a** was isolated. Both **16a** and **16b** were obtained by addition of triphenylphosphane to **14b** and to a mixture of **14a** and **15b**, respectively.

First attempts to perform the catalytic asymmetric amide cyclizations[42] previously studied by Lee et al.[19] using the newly synthesized chiral ligand gave the expected cyclization product in 70% yield and 9% *ee*. Although this result does not compare favorably with that reported in the study mentioned above, where *ee* values of up to 70% were obtained, it shows the high activity of the observed system and marks a starting point for systematic variations in the chiral ligand. Efforts to shorten the ligand synthesis while introducing sterically more demanding groups attached to the ferrocenyl moieties are currently being undertaken.

Experimental Section

General Remarks: All experiments were conducted under argon or dinitrogen using standard Schlenk-type glassware or a glovebox. Unless otherwise stated, the reactions were carried out at room temperature. All solvents were stored over activated molecular sieves (4 Å) unless otherwise indicated. In the case of freshly distilled solvents, the following drying agents were used: CaH_2 for CH_2Cl_2, MeCN, MeOH and pyridine; Na/benzophenone for pentane; Na for benzene and C_6D_6. Chromatography was carried out with Merck silica gel 60. The NMR spectra were recorded with Bruker Avance 250 (250.1 MHz, ^{1}H; 62.5 MHz, ^{13}C; 101 MHz, ^{31}P), 300 (300.1 MHz, ^{1}H; 75.0 MHz, ^{13}C; 122 MHz, ^{31}P) and 500 (500.2 MHz, ^{1}H; 125 MHz, ^{13}C; 50.7 MHz, ^{15}N; 203 MHz, ^{31}P) spectrometers. ^{1}H and ^{13}C{^{1}H} NMR chemical shifts (δ) were referenced internally by the residual solvent signal relative to tetramethylsilane. ^{31}P NMR and ^{15}N NMR chemical shifts were referenced with respect to H_3PO_4 and $MeNO_2$, respectively. All spectra were recorded at room temperature. Optical rotations were measured in 1-dm cells with a Perkin−Elmer model 341 polarimeter at 22 °C. High-resolution MALDI mass spectra were measured by the analytical service of the Laboratorium für Organische Chemie of the ETH Zürich with an IonSpec ultima FT MALDI mass spectrometer. Elemental analyses were obtained with a Leco CHN-900 analyzer. All chemicals were purchased from Fluka, Aldrich, Acros, Lancaster or ABCR and were used without further purification. (2*S*,4*S*)-2-Ferrocenyl-4-(hydroxymethyl)-1,3-dioxane,[20] (2*S*,4*S*)-2-ferrocenyl-4-(methoxymethyl)-1,3-dioxane,[20] (2*S*,4*S*,R_{Fc})-4-(methoxymethyl)-2-(2-methylferrocenyl)-1,3-dioxane (**3**),[43] (*R*)-2-methylferrocenecarboxaldehyde (**4**),[43] and ferrocenecarboxylic acid (**6b**)[22] were prepared as reported.

Benzyl *N*-Ferrocenylcarbamate (8b): Ferrocenecarboxylic acid (1.25 g, 5.43 mmol, 1.0 equiv.), Bu_4NBr (349 mg, 1.10 μmol, 0.2 equiv.) and NaN_3 (723 mg, 11.0 mmol, 2.0 equiv.) were placed in a 100-mL Schlenk flask. Addition of 35 mL of distilled CH_2Cl_2 and pyridine (1.34 mL, 1.30 g, 16.5 mmol, 3.0 equiv.) caused the formation of an orange slurry. In a separate 10-mL Schlenk flask *N*,*N*-dimethylchlorosulfitomethaniminium chloride was prepared in situ by adding thionyl chloride (0.8 mL, 11.0 mmol) to a mixture of DMF (1.0 mL, 10.2 mmol) and 5 mL of benzene. After approximately 1 min, two phases separated, with the lower one containing the desired reagent. Addition of 730 μL of the fresh, clear and colorless *N*,*N*-dimethylchlorosulfitomethaniminium chloride to the vigorously stirred orange slurry during 3 min led to a clear wine-red solution and a white precipitate (presumably Bu_4NBr). After 1 h, water was added. Extraction of the organic layer with CH_2Cl_2, followed by drying with Na_2SO_4 and evaporation of the solvents led to an intensely red-colored oil. Benzylic alcohol (6 mL) was then added and the remaining pyridine was evaporated under vac-

uum. The resulting solution of ferrocenecarboxylic azide (**7b**) in benzylic alcohol was stored in a 100-mL round-bottomed flask at room temperature under argon overnight. Upon heating to 90 °C during 30 min, the red color disappeared. The resulting brown yellowish mixture was concentrated to dryness under reduced pressure by using a distillation apparatus. A pure, orange, solid product was obtained by column chromatography (CC; CH_2Cl_2 + 1% Et_3N) on silica gel. Yield: 994 mg (55%). ^{1}H NMR ($CDCl_3$): δ = 3.99 (s, 2 H, 2 Cp_{subst}−C*H*), 4.15 (s, 5 H, Cp), 4.48 (br. s, 2 H, 2 Cp_{subst}−C*H*), 5.17 (s, 2 H, CH_2), 5.86 (br. s, 1 H, N*H*), 7.34−7.40 (m, 5 H, phenyl) ppm. MS (HR MALDI): *m*/*z* = 335.0609 (calcd. for $C_{18}H_{17}FeNO_2$); found 335.0606 [M^+]. $C_{18}H_{17}FeNO_2$ (335.18): calcd. C 64.50, H 5.11, N 4.18; found C 64.42, H 5.30, N 4.03. CAS 98639-14-6.

Aminoferrocene (9b): Compound **8b** (962 mg, 2.87 mmol, 1.0 equiv.) was suspended in 35 mL of isopropyl alcohol in a dry 100-mL Schlenk flask. After degassing the suspension in an ultrasonic bath by passing argon over it, the reaction vessel was heated to 60 °C until the substrate had dissolved completely, resulting in a clear orange solution. Pd on charcoal (10% Pd, 301 mg, 261 μmol, 0.09 equiv.) was added at room temperature and H_2 was placed over the reaction mixture. After 90 min, the solvent was removed under reduced pressure, and the residue was taken up in distilled CH_2Cl_2 and filtered. The resulting yellow solution was concentrated to dryness. The pure product was isolated as an orange solid and stored in a glovebox. Yield: 553 mg (96%). ^{1}H NMR ($CDCl_3$): δ = 2.59 (br. s, 2 H, NH_2), 3.84 (t, *J* = 1.8 Hz, 2 H, 2 Cp_{subst}−C*H*), 3.99 (t, *J* = 1.8 Hz, 2 H, 2 Cp_{subst}−C*H*), 4.10 (s, 5 H, Cp) ppm. CAS 1273-82-1.

***N*,*N*′-Diferrocenylformamidine (10b):** In a glovebox, compound **9b** (2.42 g, 12.0 mmol, 1.0 equiv.) and 1,3,5-triazine (2.92 g, 36.0 mmol, 3.0 equiv.) were placed in a dry, 500-mL round-bottomed Schlenk flask. After taking the flask out of the glovebox, 42 mL of dioxane was added, the resulting suspension was degassed in an ultrasonic bath by passing argon over it, and the reaction vessel was heated to 100 °C for 4.5 h, which led to a wine-red solution and an orange precipitate. The strong smell of ammonia upon careful opening of the reaction vessel (preventing the entry of air) indicated product formation. The reaction solvents were evaporated to dryness under reduced pressure using a distillation apparatus. At the same time, excess 1,3,5-triazine was completely sublimed, leading to an analytically pure amorphous orange solid that was stored in a glovebox. Yield: 2.37 g (96%). ^{1}H NMR ($CDCl_3$): δ = 4.04 (t, *J* = 1.8 Hz, 4 H, 4 Cp_{subst}−C*H*), 4.20 (s, 10 H, 2 Cp), 4.26 (t, *J* = 1.8 Hz, 4 H, 4 Cp_{subst}−C*H*), 8.03 (s, 1 H, N=C*H*−N) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 60.5 (Cp_{subst}−*C*H), 65.1 (Cp_{subst}−*C*H), 67.2 (Cp_{subst}−C_{quat}), 69.2 (Cp), 150.2 (N=*C*H−N) ppm. MS (HR MALDI): *m*/*z* = 412.033 (calcd. for $C_{21}H_{20}Fe_2N_2$); found 412.032 [M^+]. $C_{21}H_{20}Fe_2N_2$ (412.09): calcd. C 61.21, H 4.89, N 6.80; found C 61.15, H 4.97, N 6.68.

***N*-(2,2-Diethoxyethyl)-*N*,*N*′-diferrocenylformamidine (11b):** Compound **10b** (500 mg, 1.23 mmol, 1.0 equiv.) was suspended in 10 mL of DMF in a 50-mL Schlenk flask and cooled to 0 °C. After addition of NaH (55−65% in mineral oil, 100 mg, 2.25 mmol, 1.8 equiv.), the mixture was kept at 0 °C for 5 min and then slowly warmed to room temperature, leading to gas evolution (H_2). After 100 min stirring at room temperature 2-bromo-1,1-diethoxyethane (380 μL, 477 mg, 2.45 mmol, 2.0 equiv.) was added and the clear red solution was quickly heated to 76 °C. After 90 min, the darkened, hot mixture was concentrated to dryness under vacuum. The crude product was dissolved in MeCN followed by filtration under argon. The pure product was isolated as a clear, red oil. Yield: 515 mg (79%). ^{1}H NMR (C_6D_6): δ = 1.16 (t, *J* = 7.1 Hz, 3 H, CH_3), 1.16 (t, *J* = 7.1 Hz, 3 H, CH_3), 3.44−3.54 (m, 2 H, CH_2CH$_3$), 3.68−3.78 (m, 2 H, CH_2CH$_3$), 3.81 (t, *J* = 1.8 Hz, 1 H, Cp_{subst}−C*H*), 3.81 (t, *J* = 1.8 Hz, 1 H, Cp_{subst}−C*H*), 3.98 (t, *J* = 1.8 Hz, 1 H, Cp_{subst}−C*H*), 3.98 (t, *J* = 1.8 Hz, 1 H, Cp_{subst}−C*H*), 4.02 (s, 5 H, Cp), 4.12 (d, *J* = 5.3 Hz, 2 H, NCH_2CH), 4.19 (s, 5 H, Cp), 4.31−4.35 (m, 4 H, 4 Cp_{subst}−C*H*), 5.13 (t, *J* = 5.2 Hz, 1 H, NCH$_2$C*H*), 8.28 (s, 1 H, N=C*H*−N) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 15.6 (CH$_2$*C*H$_3$), 52.5 (N*C*H$_2$CH), 60.3 (Cp_{subst}−*C*H), 61.7 (Cp_{subst}−*C*H), 64.0 (*C*H$_2$CH$_3$), 65.0 (Cp_{subst}−*C*H), 65.2 (Cp_{subst}−*C*H), 69.0 (Cp), 100.5 (NCH$_2$*C*H), 105.5 (Cp_{subst}−C_{quat}), 108.4 (Cp_{subst}−C_{quat}), 150.6 (N=*C*H−N) ppm. MS (HR MALDI): *m*/*z* = 528.116 (calcd. for $C_{27}H_{32}Fe_2N_2O_2$); found 528.116 [M^+]. $C_{27}H_{32}Fe_2N_2O_2$ (528.25): calcd. C 61.39, H 6.11, N 5.30; found C 61.54, H 6.18, N 5.32.

***N*,*N*′-Diferrocenylimidazolium Iodide (12b):** Compound **11b** (2.38 g, 4.51 mmol, 1.0 equiv.) was dissolved in 50 mL of distilled MeCN in a dry 100-mL Schlenk flask. After addition of BF_3·OEt_2 (3.4 mL, 3.8 g, 27 mmol, 6.0 equiv.), which caused an immediate darkening of the clear, red solution, the reaction temperature was raised to 70 °C. After 3 h, additional BF_3·OEt_2 (1.7 mL, 1.9 g, 14 mmol, 3.0 equiv.) was added and the reaction mixture was stirred for 15 h. Evaporation of the solvent under reduced pressure gave a brown yellowish solid. NaI (3.38 g, 22.6 mmol, 5.0 equiv.) and 50 mL of distilled MeOH were added and the resulting mixture was stirred at 70 °C for 30 min. After evaporation of the solvent, the crude product was chromatographed on silica gel (CH_2Cl_2 + 5% MeOH) to give the pure product as a light-yellow foam. Yield: 1.92 g (75%). ^{1}H NMR ($CDCl_3$): δ = 4.34 (s, 10 H, 2 Cp), 4.36 (t, *J* = 2.0 Hz, 4 H, 2 Cp_{subst}C*H*), 5.33 (t, *J* = 2.0 Hz, 2 H, Cp_{subst}−C*H*), 7.64 (d, *J* = 1.5 Hz, 2 H, NC*H*C*H*N), 10.74 (t, *J* = 1.5 Hz, 1 H, N=C*H*−N) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 63.2 (Cp_{subst}−*C*H), 67.8 (Cp_{subst}−*C*H), 70.8 (Cp), 92.0 (Cp_{subst}−C_{quat}), 122.2 (N*C*H*C*HN), 135.1 (N=*C*H−N) ppm. MS (HR MALDI): *m*/*z* = 437.0404 (calcd. for $C_{23}H_{21}Fe_2N_2^+$); found 437.0406 [M^+ − I]. $C_{23}H_{21}Fe_2IN_2$ (564.02): calcd. C 48.98, H 3.75, I 22.50, N 4.97; found C 49.12, H 4.03, I 22.55, N 4.87.

***N*,*N*′-Diferrocenylimidazol-2-ylidene (1b):** A 20-mL Schlenk vessel was charged with compound **12b** (30 mg, 53 μmol, 1.0 equiv.) and KO*t*Bu (12 mg, 106 μmol, 2.0 equiv.) in a glovebox. Addition of 1.5 mL of distilled pentane caused the formation of an orange slurry. After stirring for 14 h, all volatiles were evaporated under reduced pressure, the residue was taken up in 1 mL of distilled deuterated benzene and filtered through a 4 Å frit. A light orange, clear solution of the product was obtained; the yield was not determined. ^{1}H NMR (C_6D_6): δ = 3.86 (t, *J* = 2.0 Hz, 4 H, 2 Cp_{subst}C*H*), 4.02 (s, 10 H, 2 Cp), 4.82 (t, *J* = 2.0 Hz, 4 H, 2 Cp_{subst}C*H*), 6.86 (s, 2 H, NC*H*C*H*N) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 62.2 (Cp_{subst}−*C*H), 65.8 (Cp_{subst}−*C*H), 69.2 (Cp), 100.4 (Cp_{subst}−*C*N), 118.9 (N*C*H*C*HN), 216.1 (N*C*N) ppm. ^{15}N NMR (C_6D_6): δ = −186.3 ppm.

***N*,*N*′-Diferrocenylimidazole-2-thione (13b):** A 20-mL Schlenk vessel was charged with compound **1b** (45 mg, 103 μmol, 1 equiv.) and S_8 (6.2 mg, 192 μmol, 2 equiv.) in a glovebox. Addition of 1 mL of distilled THF led to a brown solution and a small amount of precipitate. After 16 h, the reaction vessel was taken out of the glovebox and water was added, leading to a color change to bright yellow. The mixture was extracted with CH_2Cl_2, washed with water and dried with Na_2SO_4. ^{1}H NMR ($CDCl_3$): δ = 4.24 (t, *J* = 2.0 Hz, 4 H, 2 Cp_{subst}C*H*), 4.28 (s, 10 H, 2 Cp), 4.90 (t, *J* = 2.0 Hz, 4 H, 2 Cp_{subst}C*H*), 7.13 (s, 2 H, NC*H*C*H*N). CAS 249644-45-9.

Methyl (*R*)-2-Methylferrocenecarboxylate (5): (*R*)-2-Methylferrocenecarboxaldehyde (**4**) (6.74 g, 29.6 mmol, 1.0 equiv.) and 120 mL of MeOH were added to a 1-L flask and cooled to 0 °C. Addition of KOH (16.6 g, 296 mmol, 10 equiv.) was followed by addition of I_2 (37.5 g, 148 mmol, 5.0 equiv.). After 4 h, the solvents were evaporated under reduced pressure at 0 °C (to prevent overoxidation to the corresponding ferrocenium cation) and the remaining residue was chromatographed on silica gel (CH_2Cl_2) to give a red oil. Yield: 5.87 mg (77%). ^{1}H NMR ($CDCl_3$): δ = 2.28 (s, 3 H, Cp−C*H*$_3$), 3.81 [s, 3 H, C(O)OC*H*$_3$], 4.12 (s, 5 H, Cp), 4.23 (t, J = 2.6 Hz, 1 H, Cp_{subst}−C*H*), 4.31 (t, J = 1.6 Hz, 1 H, Cp_{subst}−C*H*), 4.71 (dd, J_1 = 2.6, J_2 = 1.6 Hz, 1 H, Cp_{subst}−C*H*) ppm. CAS 12242-23-8.

(*R*)-2-Methylferrocenecarboxylic Acid (6a): Compound **5** (7.33 g, 28.4 mmol) was dissolved in 140 mL of EtOH in a 500-mL round-bottomed flask. An aqueous solution of NaOH (70 mL, 1.1 M) was added, then the reaction mixture was stirred for 4 h at room temperature and for a further 12 h at 60 °C. Water was then added and the organic impurities were extracted with *tert*-butyl methyl ether. The aqueous phases were acidified with 0.7 M aqueous HCl and extracted with CH_2Cl_2. The organic layers were dried with $NaSO_4$, the solvent was evaporated and the product was isolated in the form of red crystals. Yield: 6.45 g (93%). ^{1}H NMR ($CDCl_3$): δ = 2.31 (s, 3 H, C*H*$_3$), 4.20 (s, 5 H, Cp), 4.31 (t, J = 2.5 Hz, 1 H, Cp_{subst}−C*H*), 4.39 (t, J = 1.9 Hz, 1 H, Cp_{subst}−C*H*), 4.80 (dd, J_1 = 2.5, J_2 = 1.8 Hz, 1 H, Cp_{subst}−C*H*) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 14.8 (*C*H$_3$), 68.1 (Cp_{subst}−*C*$_{quat}$), 69.7 (Cp_{subst}−*C*H), 70.8 (Cp), 71.0 (Cp_{subst}−*C*H), 74.4 (Cp_{subst}−*C*H), 87.7 (Cp_{subst}−*C*$_{quat}$), 178.9 (*C*OOH) ppm. CAS 12241-80-4.

Benzyl *N*-[(*R*)-2-Methylferrocenyl]carbamate (8a): Compound **6a** (4.10 g, 16.82 mmol, 1.0 equiv.), Bu_4NBr (1.09 g, 3.44 mol, 0.2 equiv.) and NaN_3 (2.26 g, 34.4 mmol, 2.0 equiv.) were placed in a 500-mL Schlenk flask. Addition of 114 mL of distilled CH_2Cl_2 and pyridine (4.18 mL, 4.07 g, 515 mmol, 3.0 equiv.) gave an orange-red solution. In a separate 10-mL Schlenk flask, *N*,*N*-dimethylchlorosulfitomethaniminium chloride was prepared in situ by adding thionyl chloride (4.6 mL, 62.9 mmol) to a mixture of DMF (5.7 mL, 58.4 mmol) and 28 mL of benzene. After approximately 1 min, two phases separated, with the lower one containing the desired reagent. Addition of 2.29 mL of the fresh, clear and colorless *N*,*N*-dimethylchlorosulfitomethaniminium chloride to the vigorously stirred orange slurry during 3 min led to a clear wine-red solution and a white precipitate (presumably Bu_4NBr). After 1 h 25 min, 23 mL of benzylic alcohol was added and the remaining dichloromethane and pyridine were evaporated under high vacuum. The resulting solution of (*R*)-2-methylferrocenecarboxylic azide (**7a**) in benzylic alcohol was stirred at 90 °C during 10 min, which caused darkening of the reaction mixture. The resulting brownish-yellow solvents were evaporated to dryness under reduced pressure during 45 min at 90 °C by using a distillation apparatus. A pure, orange, solid product was obtained by CC (CH_2Cl_2 + 1% NEt_3) on silica gel. Yield: 4.72 g (81%). ^{1}H NMR ($CDCl_3$): δ = 1.95 (s, C*H*$_3$), 3.90 (t, J = 2.5 Hz, 1 H, Cp_{subst}−C*H*), 3.95−3.97 (m, 1 H, Cp_{subst}−C*H*), 4.06 (s, 5 H, Cp), 4.62 (br. s, 1 H, Cp_{subst}−C*H*), 5.18 (s, 2 H, C*H*$_2$), 5.89 (br. s, 1 H, N*H*), 7.34−7.38 (m, 5 H, phenyl) ppm. MS (HR MALDI): *m*/*z* = 349.0765 (calcd. for $C_{19}H_{19}FeNO_2$); found 349.0757 [M^+]. $C_{19}H_{19}FeNO_2$ (349.20): calcd. C 65.35, H 5.48, N 4.01; found C 65.46, H 5.44, N 3.92. CAS 32196−69−3.

(*R*)-1-Amino-2-methylferrocene (9a): Compound **8a** (2.00 g, 5.73 mmol, 1.0 equiv.) was suspended in 35 mL of isopropyl alcohol in a dry 100-mL Schlenk flask. After degassing the suspension in an ultrasonic bath by passing argon over it, the reaction vessel was heated to 70 °C until the substrate had dissolved completely, resulting in a clear orange solution. Pd on charcoal (10% Pd, 656 mg, 573 μmol, 0.1 equiv.) was added at room temperature and H_2 was placed over the reaction mixture. After 110 min, the solvent was removed under reduced pressure, the residue was taken up in distilled CH_2Cl_2 and filtered. The resulting yellow solution was concentrated to dryness. The pure product was isolated as a bright-orange solid and stored in a glovebox. Yield: 1.23 g (quant). ^{1}H NMR (C_6D_6): δ = 1.72 (s, 3 H, C*H*$_3$), 2.03 (br. s, 2 H, N*H*$_2$), 3.66 (t, J = 2.1 Hz, 1 H, Cp_{subst}−C*H*), 3.70−3.77 (m, 2 H, Cp_{subst}−C*H*), 3.91 (s, 5 H, Cp) ppm. CAS 31760-79-9.

***N*,*N*′-Bis[(*R*)-2-methylferrocen-1-yl]formamidine (10a):** Compound **9a** (1.17 g, 5.44 mmol, 1.0 equiv.) and 1,3,5-triazine (1.32 g, 16.3 mmol, 3.0 equiv.) were placed in a dried 100-mL, round-bottomed Schlenk flask in a glovebox. After taking the flask out of the glovebox, 18 mL of dioxane was added and the resulting suspension was degassed in an ultrasonic bath by passing argon over it. The reaction vessel was then heated to 100 °C for 2.25 h, which led to a clear red solution. The strong smell of ammonia upon careful opening of the reaction vessel (preventing the entry of air) indicated product formation. The reaction solvents were evaporated to dryness under reduced pressure using a distillation apparatus. At the same time, excess 1,3,5-triazine was completely sublimed, leading to an analytically pure amorphous orange solid that was stored in a glovebox. Yield: 1.48 g (quant). ^{1}H NMR (C_6D_6): δ = 1.95 (s, 6 H, 2 C*H*$_3$), 3.81 (t, J = 2.6 Hz, 2 H, 2 Cp_{subst}−C*H*), 3.89 (t, J = 1.7 Hz, 2 H, 2 Cp_{subst}−C*H*), 4.04 (s, 10 H, 2 Cp), 4.22 (br. s, 2 H, 2 Cp_{subst}−C*H*), 7.99 (s, 1 H, N=C*H*−N) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 12.2 (C*H*$_3$), 58.8 (Cp_{subst}−*C*H), 62.3 (Cp_{subst}−*C*H), 66.6 (Cp_{subst}−*C*H), 69.1 (Cp_{subst}−*C*$_{quat}$), 69.4 (Cp), 76.5 (Cp_{subst}−*C*$_{quat}$), 150.6 (N=*C*H−N) ppm. MS (HR MALDI): *m*/*z* = 440.0638 (calcd. for $C_{23}H_{24}Fe_2N_2$); found 440.0630 [M^+]. $C_{23}H_{24}Fe_2N_2$ (440.14): calcd. C 62.76, H 5.50, N 6.36; found C 62.59, H 5.38, N 6.55. $[\alpha]_{22}$ = +1229 (c = 1, $CHCl_3$).

***N*-(2,2-Diethoxyethyl)-*N*,*N*′-bis[(*R*)-2-methylferrocen-1-yl]formamidine (11a):** Compound **10a** (1.14 mg, 2.58 mmol, 1.0 equiv.) was dissolved in 20 mL of DMF in a 100-mL Schlenk flask. The mixture was degassed in an ultrasonic bath by passing argon over it and cooled to 0 °C. After addition of NaH (55−65% in mineral oil, 203 mg, 4.64 mmol, 1.8 equiv.), the mixture was kept at 0 °C for 15 min and then slowly warmed to room temperature, leading to gas evolution (H_2). After 2 h 40 min of stirring at room temperature, 2-bromo-1,1-diethoxyethane (802 μL, 1.02 g, 5.17 mmol, 2.0 equiv.) was added and the clear red solution was quickly heated to 80 °C. After 3 h 20 min, another portion of bromoacetaldehyde diethylacetal (802 μL, 254 mg, 1.29 mmol, 0.5 equiv.) was added and stirring was continued for 90 min. The reaction solvents were evaporated to dryness under vacuum. The crude product was dissolved in distilled MeCN and filtered under argon. The pure product was isolated as a clear, red oil. Yield: 1.17 g (82%). ^{1}H NMR (C_6D_6): δ = 1.13 (t, J = 6.8 Hz, 3 H, CH_2CH_3), 1.18 (t, J = 7.0 Hz, 3 H, CH_2CH_3), 1.86 (s, 3 H, Cp−C*H*$_3$), 2.24 (s, 3 H, Cp−C*H*$_3$), 3.45−3.74 (m, 4 H, 2 CH_2CH_3), 3.74−3.77 (m, 1 H, Cp_{subst}−C*H*), 3.77−3.80 (m, 1 H, Cp_{subst}−C*H*), 3.89−3.92 (m, 1 H, Cp_{subst}−C*H*), 4.04 (s, 5 H, Cp), 4.09 (d, J = 5.5 Hz, 2 H, NC*H*$_2$CH), 4.13 (s, 5 H, Cp), 4.18−4.22 (m, 1 H, Cp_{subst}−C*H*), 4.25−4.29 (m, 1 H, Cp_{subst}−C*H*), 5.30 (t, J = 5.2 Hz, 1 H, NCH$_2$C*H*), 8.57 (s, 1 H, N=C*H*−N) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 12.9 (cp−*C*H$_3$), 13.3 (cp−*C*H$_3$), 15.6 (CH_2CH_3), 15.6 (CH_2CH_3), 53.4 (N*C*H$_2$CH), 57.7 (Cp_{subst}−*C*H), 62.6 (Cp_{subst}−*C*H), 62.7 (2 Cp_{subst}−*C*H), 63.7 (CH_2CH_3), 64.0

(CH_2CH_3), 67.0 ($Cp_{subst}-CH$), 67.2 ($Cp_{subst}-CH$), 69.8 (Cp), 70.0 (Cp), 78.8 ($Cp_{subst}-CCH_3$), 79.3 ($Cp_{subst}-CCH_3$), 99.9 (NCH_2CH), 104.7 ($Cp_{subst}-CN$), 107.2 ($Cp_{subst}-CN$), 153.3 (N=CH−N) ppm. MS (HR MALDI): m/z = 556.1476 (calcd. for $C_{29}H_{36}Fe_2N_2O_2$); found 556.1475 [M^+]. $C_{29}H_{36}Fe_2N_2O_2$ (556.30): calcd. C 62.61, H 6.52, N 5.04; found C 62.46, H 6.68, N 5.33. $[\alpha]_{22}$ = +675 (c = 1, $CHCl_3$).

***N,N′*-Bis[(*R*)-2-methylferrocen-1-yl]imidazolium Iodide (12a):** Compound **11a** (1.36 g, 2.45 mmol, 1.0 equiv.) was dissolved in 28 mL of distilled MeCN in a dry 100-mL Schlenk flask. After addition of $BF_3{\cdot}OEt_2$ (1.88 mL, 2.09 g, 14.7 mmol, 6.0 equiv.) at room temperature, which caused an immediate darkening of the reaction mixture, the reaction temperature was raised to 70 °C. After 3 h, additional $BF_3{\cdot}OEt_2$ (0.9 mL, 1.0 g, 7.0 mmol, 2.9 equiv.) was added and the reaction mixture was stirred for 15 h. Evaporation of the solvent under reduced pressure gave a brown yellowish solid. NaI (1.83 g, 12.3 mmol, 5.0 equiv.) and 28 mL of distilled MeOH were added and the resulting mixture was stirred at 70 °C for 2 h. After evaporation of the solvent, the crude product was first filtered through a silica-gel pad (CH_2Cl_2 + 5% MeOH) to remove excess NaI and borate waste, and then chromatographed on silica gel (CH_2Cl_2 + 5% MeOH) to give the product as a light-yellow foam. Yield: 1.03 g (71%). ^{1}H NMR (CD_2Cl_2): δ = 1.99 (s, 6 H, 2 CH_3), 4.28 (t, J = 2.7 Hz, 2 H, 2 Cp_{subst}−CH), 4.33 (s, 10 H, 2 Cp), 4.39−4.42 (m, 2 H, 2 Cp_{subst}−CH), 4.85 (dd, J_1 = 2.7, J_2 = 1.2 Hz, 2 H, 2 Cp_{subst}−CH), 7.85 (d, J = 1.5 Hz, 2 H, NCHCHN), 9.03 (t, J = 1.5 Hz, 1 H, N=CH−N) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 13.0 ($Cp_{subst}-CH_3$), 65.6 ($Cp_{subst}-CH$), 65.8 ($Cp_{subst}-CH$), 69.5 ($Cp_{subst}-CH$), 71.2 (Cp), 79.2 ($Cp_{subst}-C_{quat}$), 92.6 ($Cp_{subst}-C_{quat}$), 125.4 (NCHCHN), 137.3 (N=CHCHN) ppm. MS (HR MALDI): m/z = 465.0717 (calcd. for $C_{25}H_{25}Fe_2N_2^+$); found 465.0715 [M^+ − I]. $C_{25}H_{25}Fe_2IN_2$ (592.07): calcd. C 50.71, H 4.26, N 4.73; found C 50.93, H 4.49, N 4.68. $[\alpha]_{22}$ = +104 (c = 1, $CHCl_3$).

***N,N′*-Bis[(*R*)-2-methylferrocen-1-yl]imidazol-2-ylidene (1a):** A 20-mL Schlenk vessel was charged with compound **12a** (20 mg, 34 μmol, 1.0 equiv.) and KO*t*Bu (8 mg, 71 μmol, 2.1 equiv.) in a glovebox. Addition of 2 mL of distilled pentane caused the formation of an orange slurry. After stirring for 3.5 h, all volatiles were evaporated under reduced pressure, the residue was taken up in 1 mL of distilled deuterated benzene and filtered through a 4 Å frit, which led to a clear light-yellow solution. ^{1}H NMR (C_6D_6): δ = 2.26 (s, 6 H, 2 CH_3), 3.81 (t, J = 2.5 Hz, 2 H, 2 Cp_{subst}CH), 3.90 (t, J = 2.0 Hz, 2 H, 2 Cp_{subst}CH), 4.07 (s, 10 H, 2 Cp), 4.38−4.40 (m, 2 H, 2 Cp_{subst}CH), 7.01 (s, 2 H, NCHCHN) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 14.5 ($Cp_{subst}-CH_3$), 63.6 ($Cp_{subst}-CH$), 64.2 ($Cp_{subst}-CH$), 68.0 ($Cp_{subst}-CH$), 70.0 (Cp), 79.6 ($Cp_{subst}-CCH_3$), 99.8 ($Cp_{subst}-CN$), 120.8 (NCHCHN), 221.2 (NCN) ppm. ^{15}N NMR (C_6D_6): δ = −188.2 ppm.

***N,N′*-Bis[(*R*)-2-methylferrocen-1-yl]imidazole-2-thione (13a):** S_8 (4.1 mg, 128 μmol, 3.5 equiv.) was added to the solution of compound **1a** in benzene prepared above. After a reaction time of 30 min, ^{1}H NMR analysis of the solution showed complete and clean conversion. ^{1}H NMR (C_6D_6): δ = 1.94 (s, 6 H, 2 CH_3), 3.79 (t, J = 2.5 Hz, 2 H, 2 Cp_{subst}CH), 3.86 (t, J = 2.1 Hz, 2 H, 2 Cp_{subst}CH), 3.98 (s, 10 H, 2 Cp), 4.49−4.51 (m, 2 H, 2 Cp_{subst}CH), 7.01 (s, 2 H, NCHCHN) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 13.5 ($Cp_{subst}-CH_3$), 64.6 ($Cp_{subst}-CH$), 67.6 ($Cp_{subst}-CH$), 68.0 ($Cp_{subst}-CH$), 70.1 (Cp), 81.7 ($Cp_{subst}-CCH_3$), 96.5 ($Cp_{subst}-CN$), 119.6 (NCHCHN), 170.3 (NCN) ppm. MS (HR MALDI): m/z = 496.0359 (calcd. for $C_{25}H_{24}Fe_2N_2S$); found 496.0359 [M^+].

Palladium Complex 14b: Compound **12b** (200 mg, 354 μmol, 1.0 equiv.) and $[Pd(OAc)_2]_3$ (79.6 mg, 351 μmol, 1.0 equiv.) were dissolved in 7 mL of distilled pyridine in a dry 20-mL Schlenk flask. The resulting yellow solution was stirred for 3 h, then NaI (270 mg, 1.80 mmol, 5.1 equiv.) was added, leading to a color change to brown and the formation of a precipitate (other than NaI). After 18 h of stirring, all volatiles were evaporated under reduced pressure. The pure orange product was obtained by CC (CH_2Cl_2) on silica gel. Yield: 160 mg (59%). ^{1}H NMR (C_6D_6): δ = 3.99 (t, J = 1.9 Hz, 4 H, 2 Cp_{subst}-CH), 4.10 (s, 10 H, 2 Cp), 5.50 (t, J = 1.8 Hz, 4 H, 2 Cp_{subst}−CH), 6.22−6.26 (m, 2 H, py), 6.53 (tt, J_1 = 1.8, J_2 = 7.8 Hz, 1 H, py), 7.03 (s, 2 H, NCHCHN), 8.98−9.00 (m, 2 H, py) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 66.3 ($Cp_{subst}-CH$), 66.6 ($Cp_{subst}-CH$), 70.1 (Cp), 97.7 ($Cp_{subst}-C_{quat}$), 123.5 (NCHCHN), 123.9 (py), 136.8 (py), 151.1 (N−CPd−N), 154.4 (py) ppm. MS (HR MALDI): m/z = 795.7450 (calcd. for $C_{23}H_{20}Fe_2N_2I_2Pd$); found 795.7470 [M − py]$^+$ with the expected isotopic pattern. $C_{28}H_{25}Fe_2I_2N_3Pd$ (769.02): calcd. C 38.37, H 2.99, N 4.79, I 28.96; found C 38.57, H 3.08, N 4.59, I 29.08.

Palldium Complexes 14a and 15a: Compound **12a** (100 mg, 169 μmol, 1.0 equiv.) and $[Pd(OAc)_2]_3$ (38.0 mg, 169 μmol, 1.0 equiv.) were dissolved in 5 mL of distilled pyridine in a dry 20-mL Schlenk flask. The resulting clear, brown solution was stirred for 3.5 h, then NaI (132 mg, 879 μmol, 5.2 equiv.) was added to the darkened mixture, which caused a slight lightening of the color and the formation of a precipitate (other than NaI). After 15 h of stirring, all volatiles were evaporated under reduced pressure. An orange mixture of the two products was obtained by CC (CH_2Cl_2) on silica gel. Yield: 106 mg (54%). The mixture consists of 53.5 mg (59.2 μmol) of the mononuclear and 52.3 mg (31.7 μmol) of the dinuclear species, as determined by ^{1}H NMR spectroscopy. ^{1}H NMR (C_6D_6; resonances that belong to **14a** are designated with M, those belonging to **15a** with D): δ = 1.69 (s, 6 H, 2 CH_3, D), 2.01 (s, 6 H, 2 CH_3; D), 2.11 (s, 6 H, 2 CH_3, M), 3.86 (s, 10 H, 2 Cp, D), 3.92 (s, 10 H, 2 Cp, D), 3.97 (s, 10 H, 2 Cp, M), 4.02 (t, J = 2.6 Hz, 2 H, 2 Cp_{subst}−CH, M), 4.27 (t, J = 2.5 Hz, 2 H, 2 Cp_{subst}−CH, D), 5.64−5.68 (m, 2 H, 2 Cp_{subst}−CH, D), 5.71−5.75 (m, 2 H, 2 Cp_{subst}−CH, D), 6.00 (dd, J_1 = 2.5, J_2 = 1.0 Hz, 2 H, 2 Cp_{subst}−CH, M), 6.10−6.17 (m, 2 H, py, M), 6.39−6.48 (m, 1 H, py, M), 7.19−7.22 (m, 2 H, NCHCHN, D), 7.34 (s, 2 H, NCHCHN, M), 8.76−8.81 (m, 2 H, py, M) ppm.

Palladium Complex 16a: Addition of 1.5 mL of CH_2Cl_2 to a dry 20-mL Schlenk flask containing a mixture of **14a** and **15a** (97 mg, 123 μmol Pd^{II}, 1.0 equiv.) and triphenylphosphane (60.2 mg, 230 μmol, 2.8 equiv.) caused the formation of a clear red to orange solution. After 1 h of stirring, all volatiles were removed under reduced pressure and the residue was rinsed five times with pentane. Drying under reduced pressure yielded a pale-yellow solid. Yield: 115 mg (86%). ^{1}H NMR (CD_2Cl_2): δ = 2.08 (s, 6 H, 2 CH_3), 4.27−4.30 (m, 14 H, 2 cp and 4 Cp_{subst}−CH), 5.34 (t, 2 H, 2 Cp_{subst}−CH, J = 2.0 Hz), 7.29−7.33 (m, 6 H, PPh_3), 7.34−7.40 (m, 3 H, PPh_3), 7.43−7.49 (m, 6 H, PPh_3), 7.72 (d, 2 H, J = 1.0 Hz, NCHCHN) ppm. ^{13}C NMR (CD_2Cl_2): δ = 13.1 ($Cp_{subst}-CH_3$), 64.0 ($Cp_{subst}-CH$), 68.1 ($Cp_{subst}-CH$), 68.7 ($Cp_{subst}-CH$), 70.0 (Cp), 79.3 ($Cp_{subst}-CN$), 97.9 ($Cp_{subst}-CCH_3$), 124.6 (d, J = 5.6 Hz, (NCHCHN), 127.5 (d, J = 10.1 Hz, PPh_3), 129.9 (d, J = 2.3 Hz, PPh_3), 133.0 (d, J = 44.3 Hz, PPh_3), 135.4 (d, J = 11.0 Hz, PPh_3), 165.2 (d, J = 193.7 Hz, N−CPd−N) ppm. ^{31}P NMR (CD_2Cl_2): δ = 17.7 ppm. MS (HR MALDI): m/z = 958.9629 (calcd. for $C_{43}H_{39}Fe_2IN_2PPd$); found 958.9654 [M − I$^+$] with the expected isotopic pattern. $C_{43}H_{39}Fe_2I_2N_2PPd$ (1086.68): calcd. C 47.53, H 3.62, I 23.36, N 2.58, P 2.85; found C 47.60, H 3.73, I 23.11, N 2.51, P 3.02. $[\alpha]_{22}$ = +79 (c = 1, $CHCl_3$).

Table 1. X-ray crystallographic data of **12a**, **12b** and **16a**

	12a	**12b**	**16a**
Empirical formula	$C_{25}H_{25}Fe_2IN_2$	$C_{23}H_{21}Fe_2IN_2$	$C_{43}H_{39}Fe_2I_2N_2PPd$
Formula mass	592.07	564.02	1086.63
Temperature [K]	200(2)	298(2)	293(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	triclinic	orthorhombic	monoclinic
Space group	*P*1	*Pnma*	$P2_1$
Unit cell dimensions	a = 9.0692(7) Å	a = 7.1601(4) Å	a = 10.299(3) Å
	b = 25.0236(19) Å	b = 7.5642(4) Å	b = 11.827(3) Å
	c = 9.1270(7) Å	c = 10.9701(6) Å	c = 16.900(4) Å
	α = 90°	α = 84.6960(10)°	α = 90°
	β = 90°	β = 85.4760(10)°	β = 99.772(5)°
	γ = 90°	γ = 73.4130(10)°	γ = 90°
Volume [Å^3]	566.13(5)	2071.3(3)	2028.7(9)
Z	1	4	2
Calcd. density [g/cm^3]	1.737	1.809	1.779
Absorption coefficient [mm^{-1}]	2.659	2.902	2.738
Crystal size [mm]	0.39 × 0.23 × 0.14	0.21 × 0.08 × 0.05	0.60 × 0.28 × 0.23
Reflections collected, unique	5840, 5118	12775, 2172	20853, 9926
R_{int}	0.0114	0.0346	0.0253
Refinement method		full-matrix least squares on F^2	
Data, restraints, parameters	5118, 3, 273	2172, 0, 130	9926, 1, 462
GOF	1.057	1.322	1.048
R, R_w	0.0214, 0.0531	0.0822, 0.1525	0.0290, 0.0635
Min./max. residual [e·Å^{-3}]	0.695/−0.287	1.706/−1.334	0.994/−0.505

Palladium Complex 16b: A 100-mL Schlenk vessel was charged with compound **14b** (157 mg, 204 μmol, 1.0 equiv.) and triphenylphosphane (107 mg, 408 μmol, 2.0 equiv.). After addition of 3.0 mL of CH_2Cl_2, the cloudy orange mixture turned into a clear yellow solution within 5 min. After 2 h, the solvent was evaporated under reduced pressure, and the product was separated from excess PPh_3, as a yellow powder, by repeated washing with pentane. Yield: 195 mg (94%). ^{1}H NMR (CD_2Cl_2): δ = 4.26−431 (m, 14 H, 2 cp and 2 Cp_{subst}−*C*H), 5.18 (t, J = 2.0 Hz, 2 Cp_{subst}−*C*H), 7.24−7.61 (m, 15 H, PPh_3), 7.58 (d, J = 1.2 Hz, 2 H, NC*HCH*N) ppm. ^{13}C NMR (CD_2Cl_2): δ = 65.6 (Cp_{subst}−*C*H), 66.1 (Cp_{subst}−*C*H), 69.7 (Cp), 97.3 (d, J = 0.8 Hz, Cp_{subst}−*C*N), 123.6, (d, J = 5.6 Hz, (N*CHCH*N), 127.6 (d, J = 10.2 Hz, PPh_3), 130.0 (d, J = 2.3 Hz, PPh_3), 132.7 (d, J = 44.4 Hz, PPh_3), 135.2 (d, J = 10.9 Hz, PPh_3), 159.8 (d, J = 189.9 Hz, N−*C*Pd−N) ppm. ^{31}P NMR (CD_2Cl_2): δ = 16.7 ppm. MS (HRes MALDI): m/z = 930.9316 (calcd. for $C_{41}H_{35}Fe_2IN_2PPd$); found 930.9334 [M − I$^+$] with the expected isotopic pattern. $C_{41}H_{35}Fe_2I_2N_2PPd$ (1058.64): calcd. C 46.52, H 3.33, N 2.65; found C 47.30, H 3.44, N 2.63.

X-ray Crystallographic Study: X-ray structural measurements were carried out with a Bruker CCD diffractometer (Bruker SMART PLATFORM, with CCD detector, graphite monochromator, Mo-K_α radiation). The program SMART was used for data collection. Integration was performed with SAINT. The structure solution and refinement on F^2 were accomplished with SHELXTL 97. Model plots were made with ORTEP32. All structures were solved by direct methods. All non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were refined at calculated positions riding on their carrier atoms. Weights were optimized in the final refinement cycles. A summary of the most important crystallographic data is given in Table 1. CCDC-239875 (**12b**), -239876 (**16a**) and -239877 (**12a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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