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Synthesis of substituted 1,1′-diaminoferrocenes from cyclo-2-pentene imines

Katharina R. Nikolaides, Stephan D. Hoffmann, Jörg Eppinger *

Technische Universität München, Department Chemie, Lichtenbergstr. 4, D-85747 Garching, Germany

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Abstract

Condensation of anilines and primary aliphatic amines with 3,4-diphenylcyclo-2-pentenone leads to the corresponding diphenylcyclopentene imines in good yields of 72–90%. Deprotonation of these aminocyclopentadiene tautomers and reaction with $FeCl_2$ leads to the synthesis of the respective 1,1′-diamino-3,3′,4,4′-tetraphenylferrocenes. Yields increase from 33% to 65% with a decrease in the steric bulk of the amine substituent. The observation that a successful conversion requires two equivalents of base is conceived on the basis of the discussed reaction mechanism. The molecular structure of 1,1′-dianilino-3,3′,4,4′-tetraphenylferrocene (**3a**), which was determined by single crystal X-ray analysis reveals a *trans* coordination of the two amine moieties with respect to the central Cp–Fe–Cp axis of the ferrocenyl backbone.

Keywords: Ferrocene; Aminoferrocene; Diamines; Silylamide route

1. Introduction

During the last decades, the unique characteristics of ferrocene derivatives have attracted considerable attention in material sciences [1] and catalysis [2]. In general, the ferrocenyl backbone is set apart from purely organic moieties by three properties [3]: (i) chemical stability and electrochemical reversibility of the ferrocene/ferrocinium redox couple, (ii) electronic stabilisation of adjacent electron-deficient centers due to participation of the iron atom in the dispersal of positive charge and (iii) unique steric bulk due to the cylindrical shape enabling planar chirality and a rare co-planar arrangement of substituents. While especially the last property has founded the success of ferrocene-derived chelating phosphine ligands in homogeneous catalysis [2], the homologue amines have been rarely applied [4] despite several reports emphasis interesting applications [5,6]. Especially 1,1-diaminoferrocenes were proven to be good ligands for the stabilisation of early transition metal centers applied in the polymerisation of olefins [6,7]. The main obstacle for a broader application of this class of compounds is the lack of an efficient synthetic access. Nearly all synthetic routes to di-nitrogen substituted ferrocenes proceed via a diiodo- or dibromoferrocene [3], which is subsequently either coupled with amides by an copper-mediated Ullman type reaction [8] or converted to 1,1′-diaminoferrocene [9]. This highly air sensitive compound may be derivatised by a variety of methods, e.g. by Hartwig–Buchwald coupling [10], reactions with electrophiles [11] or condensation with carbonyl functionalities [12]. However, the functionalisation of the ferrocene moiety is always achieved on the level of the dihalogenoferrocene precursors. Correspondingly, all procedures above necessitate multiple successive synthetic steps and share the lack of flexibility with respect to a functionalisation of the ferrocenyl backbone. An interesting alternative provides the method introduced by Plenio et al. [13], which utilizes a retro-synthetically different approach (Fig. 1): the assembly of 1,1-diaminoferrocenes in one step from aminocyclopentadienes and an iron(II)

* Corresponding author. Tel.: +49 (0) 89 289 13097; fax: +49 (0) 89 289 13473.
E-mail address: joerg.eppinger@ch.tum.de (J. Eppinger).

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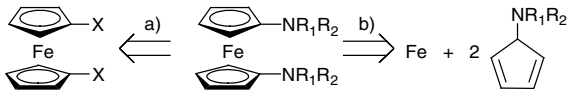
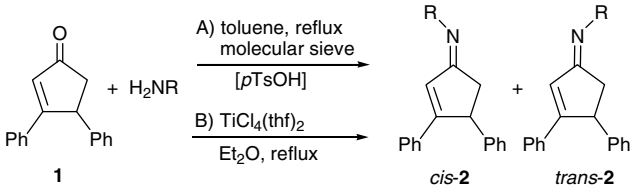


Fig. 1. Retro-synthetic conception of possible synthetic routes to 1,1′ diaminoferrocenes: (a) *via* dihalogenoferrocenes and (b) *via* aminocyclopentadienes.

precursor. However, this method so far provided an access only to *tertiary* diamines with an ferrocenyl backbone, since secondary aminocyclopentadienes are not synthetically accessible, yet. We now herein describe the expansion of the one-step assembly of a fully functionalised ferrocene to the synthesis of 1,1′-diaminoferrocenes with secondary amino groups, which offer an N–H for further derivatisations.



Compnd.	R	Yield (A) %	Yield (B) %	cis/trans
2a	C_6H_5	85	90	1.4/1
2b	4-MeC_6H_5	75	-	1.8/1
2c	2,4,6-$Me_3C_6H_2$	77	58	3.5/1
2d	2,6-$iPr_2C_6H_3$	72	47	4.2/1
2e	C_6H_5CHMe	84	-	>20/1

Scheme 1. Synthesis of the cyclo-2-pentene imines **2a**–**e**.

2. Results and discussion

Since most examples of successfully applied secondary diaminoferrocenes as ligands in homogeneous catalysis bear arene substituents at the nitrogen, we were primarily interested in a coupling of anilines to the ferrocenyl backbones. To the best of our knowledge, secondary aminocyclopentadienes have not been described, so far. Therefore, we initially intended to use the benzylamino group as a synthon, which provides a N–H functionality after hydrogenolysis. We thus attempted to react the readily available 3,4-diphenylcyclo-2-pentenone (**1**) [14] with benzylaniline under conditions that are established for the enamine reaction of *sec*-amines with cyclo-2-pentenones [13]. However, not even azeotropic distillation in high boiling solvents such as toluene or xylene yielded significant amounts of products after 48 h. The combination of decreased nucleophilicity of the arylamine and the steric bulk of the secondary amino group seems to result in a dramatically reduced reaction rate. Thus we reconsidered our approach and decided to modify the strategy towards the condensation of cyclopentenone **1** with primary amines to cyclo-2-pentene imines, which represent potential precursors since they are tautomers of secondary aminocyclopentadienes.

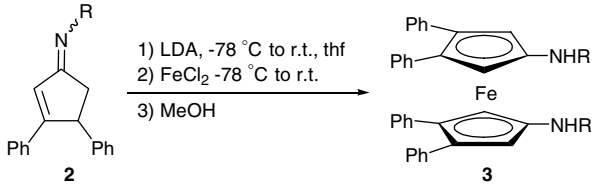
2.1. Synthesis of cyclo-2-pentene imines

Up to our work, only two publications existed, which describe cyclo-2-pentene imines [15]. However, in these reports these imines are formed and stabilised by coordination to a $W(CO)_5$-fragment. We considered the condensation of a cyclo-2-pentenone with primary amines to be a more practicable access to this class of compounds and thus reacted 3,4-diphenylcyclo-2-pentenone (**1**) with the different amines listed in Scheme 1 in the presence of catalytic amounts of acid. Generally, the reaction only proceeds at a satisfactory rate in refluxing toluene, with the *ortho*-substituted mesityl- and 2,6-diisopropylamine necessitating reaction times of up to 24 h. The reaction is driven to completion by azeotropic removal of the reaction water. At this, we received superior results when the conventional water separation funnel was replaced by a container filled with molecular sieve (4 Å) positioned between the reflux condenser and the reaction vessel. This procedure allows to synthesise the cyclopentene imines **2a**–**e** in yields of 72–85%. Care has to be taken to strictly exclude air from the condensation reaction, since oxygen seems to promote the formation of highly coloured, unwanted side product. In principle, all primary amines can be used in this synthesis. However, since sterically demanding amines require long reaction times harsh heating we sought for a method to reduce the reaction temperature, which might enable the conversion of less thermo-stable amines. Replacing the acid catalyst by stochiometric amounts of $TiCl_4(thf)_2$ as Lewis acid and oxygen trap allows to perform the synthesis of the cyclopentene imines **2a**–**e** in refluxing diethyl ether. However, the large amount of titanium(IV) by-products complicates the work-up procedure. The necessary aqueous removal of salt by-products decreases the isolated yields due to reversal of the imine formation in the presence of water.

^1H and ^{13}C NMR spectra of the cyclo-2-pentene imines obtained reveal a mixture of the *cis*- and *trans*-isomers (*cis*/*trans*-ratio = 1.4 (**2a**), 1.8 (**2b**), 3.5 (**2c**) and 4.2 (**2d**)) whereas for product **2e** only the *cis*-configuration can be detected. MM2 calculations [16] reveal that the arene substituent at the nitrogen has an energetically more disadvantageous steric interactions with the methylene group (*trans*-isomer) then with the methine moiety (*cis*-isomer). The calculated trend for the *cis*/*trans*-ratios of 1.6/1 (**2a** and **2b**), 3.9/1 (**2c**) and 14.7/1 (**2d**) at reaction temperature (120 °C) is in good agreement with the spectroscopic results. The NMR spectra of the cyclo-2-pentene imines **2c** and **2d** feature non-equivalent signals for the *ortho*-methyl (**2c**) and isopropyl (**2d**) groups, as a result of a hindered rotation around the C_{aryl}–N bond of the substituted aniline moiety.

2.2. Synthesis of 1,1′-diaminoferrocenes

We anticipated, that after deprotonation of cyclopentene imines with strong bases in THF, the resulting anion would be in equilibrium with the corresponding tautomeric aminocyclopentadienyl anion, which should react with $FeCl_2$ to yield the desired 1,1′-diaminoferrocenes. However, using *n*-BuLi, *t*-BuLi or LDA as deprotonating agent, neither after conventional deprotonation at −78 °C and reaction at room temperature, nor after prolonged reaction times and refluxing any formation of product could be detected. Thus we investigated several reaction parameters using the imine **2a** as test system (Scheme 2). Remarkably, product formation strongly depends on the amount of added base. As illustrated in Fig. 2, significant product formation is only seen for more then two equivalents of base. This observation leads us to the following interpretations (Scheme 3): (i) the desired tautomeric rearrangement of the initial deprotonation product does not take place; (ii) addition of a second equivalent of base results in a double deprotonated intermediate, which now provides an lithium cyclopentadienies contact ion pair which can readily undergo *trans*-metallation with the added iron(II) salt. Unfortunately, any attempt to isolate the assumed dilithio intermediate failed and addition of one or two equivalents of electrophiles (acyl chloride, trimethylsilyl chloride and ^{2}HCl) at low temperatures yielded inseparable mixtures of products.



Scheme 2. Synthesis of the diaminoferrocenes **3a**–**e**.

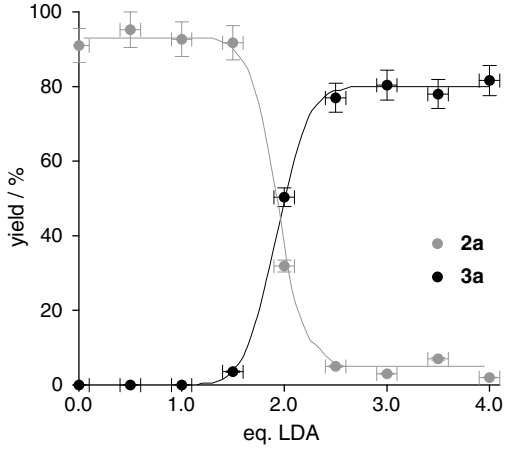
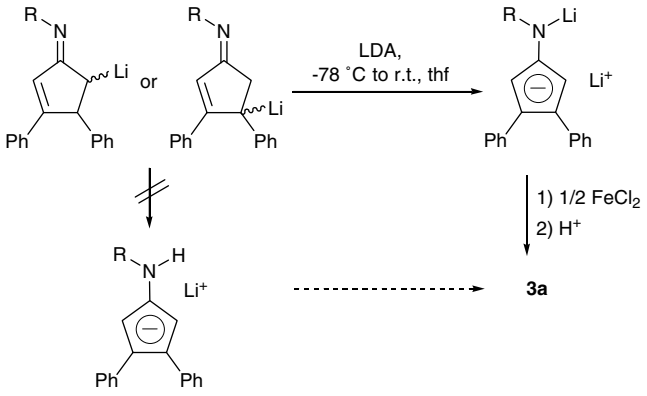


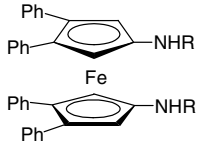
Fig. 2. Dependence of conversion of the cyclopentene imine **2a** to the 1,1′-diaminoferrocene **3a** on the amount of base added. Reaction conditions: see Scheme 2.



Scheme 3. Mechanism proposed for the formation of diaminoferrocenes from cyclo-2-pentene imines *via* a double deprotonated intermediate.

The deprotonation of the cyclopentene imines **2a**–**e** with LDA and successive addition of $FeCl_2$ leads to the formation of the respective aminoferrocenes **3a**–**e** (Chart 1). However, the reaction times required as well as side product formation increase significantly with the steric bulk of the nitrogen substituent. Correspondingly, the isolated yields for the phenyl and 4-tolyl compounds are around 65% while the mesityl, the 2,6-diisopropyl and the 1-phenylethyl derivates can only be obtained in moderate yields. Since the first products are collected as highly air sensitive dilithio-salts, strict exclusion of oxygen is mandatory for a successful isolation. Only the neutral 1,1′-diamnioferrocenes **3a**–**e** received after careful protonation are fairly stable if exposed to air. Trials with other bases then LDA did not lead to any improvements. While the use of KO*t*-Bu and $K[N(SiMe_3)_2]$ did not yield any product, presumably since the weaker bases do not achieve the necessary double deprotonation, strongly alkyl lithium bases such as *n*-BuLi or *t*-BuLi lead to the enhanced dimerisation of the cyclopentene imines.

To change from the required strongly basic to milder conditions, we investigated the possibility of adapting the silylamide route which we had already applied successfully for the synthesis of rare earth metallocenes [17]. We reasoned, that coordination of the cyclopentene imine to an undercoordinated iron precursor should facilitate the rearrangement of the π-system to an cyclopentadiene intermediate, which then could be deprotonated by the silylamine. We thus chose $Fe[N(SiMe_3)_2]_2(thf)$ [18] as iron source, which has already been applied as precursor for the synthesis of chelating *N*-heterocyclic dicarbene complexes of iron (II) [19]. Despite that sterically and electron-



3a	R= C_6H_5
3b	R = 4-MeC_6H_5
3c	R = 2,4,6-$Me_3C_6H_2$
3d	R = 2,6-$iPr_2C_6H_3$
3e	R = C_6H_5CHMe

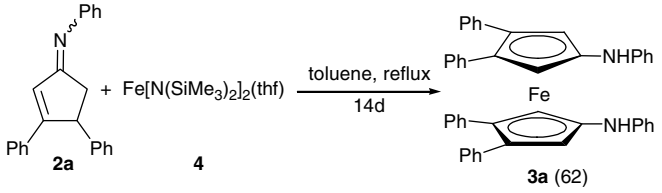
Chart 1. Summery of the synthesised diaminoferrocenes.

ically unsaturated precursor, conversion of the cyclopentene imine **2a** was very slow even in refluxing toluene. Yet, after a reaction time of 14 days, the diaminoferrocene **3a** was isolated in 62% yield (Scheme 4). Attempts to convert the sterically demanding imines **2c** and **2d** by the same method did not yield any significant amount of product.

Cyclic voltammetric studies in acetonitrile solution reveal the negative reversible one-electron oxidation, which is typical for aminoferrocenes [7,20]. The introduction of two phenyl substituents at the ferrocenyl backbone make the oxidation more difficult ($E^{0\prime}$ versus ferrocene = −0.33 V (**3a**) compared to −0.41 V for bis-1,1′-diphenylaminoferrocene [7]). This explains the observation that the diaminoferrocenes **3a**–**d** are fairly stable if exposed to air. Even at slow scan rates of 10 mV/s the oxidation of **3a** remains fully reversible, which indicates, that the oxidized complex does not decompose within the minutes time scale.

2.3. Structure analysis of *3a*

The solid structure of the aniline derivate **3a** was determined by X-ray structure analysis. Crystals suitable for X-ray diffraction studies were grown by diffusion of hexane into a saturated chloroform solution of **3a** at room temperature. Diaminoferrocene **3a** crystallises in the monoclinic space group $P2_1/c$. The solid state structure (Fig. 3) reveals that both amino substituents are oriented in the sterically



Scheme 4. Synthesis of **3a** from an iron(II) silylamide precursor (silylamide route).

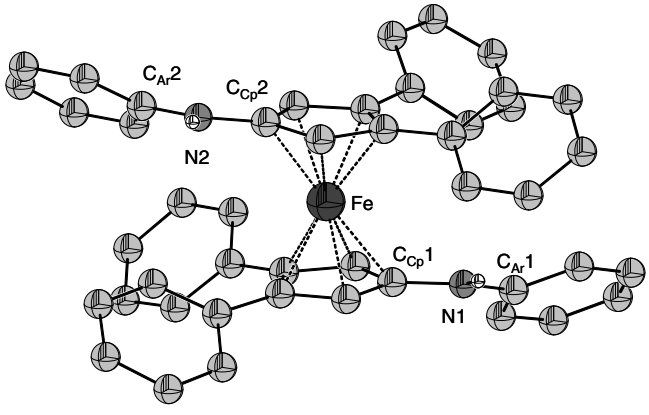


Fig. 3. Crystal structure of the diaminoferrocene **3a** (except for N–H are all hydrogens omitted for clarity). Representative distances (pm) and angles (°): $d_{average}$Fe–C_{Cp} = 2.054, Fe–C_g1 = 1.669(2), N1–$C_{Cp}1$ = 1.403(11), N2–$C_{Cp}2$ = 1.410(10), C_g1–Fe–C_g2 = 176.9(2), $C_{Ar}1$–N1–$C_{Cp}1$ = 129.2(8), $C_{Ar}2$–N2–$C_{Cp}2$ = 127.3(9); C_g: ring center and C_{Ar}: phenyl carbon at the N-atom.

more favorable *trans* conformation. A pseudo-C_2-symmetry of the diaminoferrocene core (axis through Fe-atom defined by section of the plane perpendicular to both N–C_{Cp}-axis and the plane (idealized) parallel to both Cp rings) is broken by the orientation of the tilted phenyl substituents. They are twisted into different directions for both cyclopentadienyl ring, which results in a double-propeller structure without helical chirality. The steric interaction of the phenyl rings does not cause any significant barriers for the rotation of the cyclopentadienyl rings, since neither rotamers nor significant signal broadening is evident by ^{1}H NMR spectroscopy in solution in a temperature range from −50 to +90 °C (d_8-toluene). A slight tilting of the cyclopentadienyl rings by 3.1(2)° is common for substituted ferrocenes. All distances and angles are in a range, which is typical for aminoferrocenes. Correspondingly, the N–C_{Cp} bond length are relatively short (N1–$C_{Cp}1$ = 1.403(11), N2–$C_{Cp}2$ = 1.410(10) pm). The C_{Ar}–N–C_{Cp}-angles are opened ($C_{Ar}1$–N1–$C_{Cp}1$ = 129.2(8)°, $C_{Ar}2$–N2–$C_{Cp}2$ = 127.3(9)°), reducing the steric pressure between the aniline and the bulky ferrocene moiety.

3. Conclusion

We have shown, that the condensation of a variety of primary amines with cyclo-2-pentenones under acid catalysis affords the corresponding cyclo-2-pentene imines of flexible substitution patterns in good yields. Conversion of these cyclo-2-pentene imines into the corresponding 1,1′-diaminoferrocenes requires the addition of two equivalents of base. This result can be understood by assuming, that a double deprotonation is essential for the formation of the reactive anionic cyclopentadienyl species. The silylamide route could be adapted to the synthesis of 1,1′-dianilinoferrocenes using Fe[$N(SiMe_3)_2$]$_2$(thf) as iron(II) precursor. We believe, that the facile access to diaminoferrocenes with secondary amino groups, which offer an N–H for further derivatisation reactions will open the door for substantial advances in the application of these compounds as ligands for homogeneous catalysts.

4. Experimental

4.1. General procedures

Commercially available solvents and reagents were purified according to literature procedures. All reactions were carried out in dry solvents under an argon atmosphere. NMR spectra were recorded at 300 K with a Bruker DPX 400 (^{1}H NMR 400.13 MHz, ^{13}C NMR 100.61 MHz). ^{1}H NMR were referenced to the residual ^{1}H-impurities in the solvent, and ^{13}C NMR, to the solvent signals: $CDCl_3$ (7.24 ppm, 77.0 ppm), C_6D_6 (7.15 ppm, 128.0 ppm), d_8-THF (3.73 ppm, 1.71 ppm; 68.6 ppm 26.7 ppm). Signals that overlap with solvent signals are indicated by a cross (#). Mass spectra: Finnigan MAT 90. IR spectra: Perkin–Elmer 1650 FTIR; solid materials

as KBr tablets. Element analyses: Mikroanalytisches Laboratorium der Technischen Universität München. 3,4-Diphenylcyclo-2-pentenone [14] and $Fe[N(SiMe_3)_2]_2(thf)$ [18] were synthesised according to the literature procedures. Cyclic voltammetry: the standard electrochemical instrumentation consisted of a Princeton Applied Research potentiostat/galvanostat (model 273A). Cyclic voltammograms were recorded in dry CH_3CN under an argon atmosphere at ambient temperature. A three-electrode configuration was employed. The working electrode was a Pt disk (diameter 1 mm) sealed in soft glass, and the counter electrode, a Pt disk (area 3 cm^2). Solutions were ca. 1×10^{-3} mol dm^{-3}. $(NBu_4)ClO_4$ (0.2 M) was used as a supporting electrolyte.

4.2. Synthesis

4.2.1. General procedure for the synthesis of cyclo-2-pentene imines **2a**–**2e**

Route A (acid catalysed): Cyclo-2-pentenone (1 eq.), amine (3 eq.), *p*-toluenesulfonic acid (0.05 eq.) were dissolved in toluene (2 mL/mmol) under argon atmosphere and the resulting mixture was refluxed through a mol sieve (4 Å) container at 120–140 °C for the time mentioned. Reaction always is accompanied by a colour change to green. After the reaction mixture was cooled to room temperature all volatiles were removed in vacuum (10^{-3} mbar) and the remaining solid was re-crystallised from diethyl ether.

Route B ($TiCl_4$-mediated): Cyclo-2-pentenone (1 eq.) and amine (6 eq.) were dissolved in diethyl ether (3.5 mL/mmol) under argon atmosphere before $TiCl_4(thf)_2$ (1.09 eq.) was added as a yellow solid. The reaction mixture was then refluxed for 48 h. The mixture was cooled to room temperature, evaporated to dryness, re-dissolved in ethyl acetate and transferred into a separating funnel. The organic layer was than twice extracted with 5% glacial acid, twice with saturated aqueous NaOAc and washed with brine. The organic layer was separated and dried over $MgSO_4$ and the volatiles were evaporated. The crude product was washed with hexane, re-crystallised from ether and dried under vacuum.

4.2.2. N-phenyl-3,4-diphenylcyclo-2-pentene imine (**2a**)

Route A reagents: 3,4-Diphenylcyclo-2-pentenone 1 (1.50 g, 6.40 mmol), aniline (1.86 g, 20 mmol), *p*-toluenesulfonic acid (75.0 mg, 0.32 mmol), reaction time: 1 h, yield: 1.68 g (85%), green powder. *Route B reagents:* 3,4-Diphenylcyclo-2-pentenone 1 (4.50 g, 19.2 mmol), aniline (10.7 g, 115.2 mmol), $TiCl_4(thf)_2$ (7.0 g, 20.9 mmol), yield: 5.35 g (90%), pale-green powder. ^{1}H NMR ($CDCl_3$): *cis*/*trans* = 1.4/1; *cis*-isomer: $\delta = 7.55$–6.83 (m, 16H, Ar*H* + CNC*H*), 4.54 (d, $J = 7.3$ Hz, 1H, PhC*H*CH_2), 3.13 (dd, $J = 7.4$, 18.8 Hz, 1H, *trans*-PhCHCH_2), 2.46 (dd, $J = 2.0$, 18.8 Hz, 1H, *cis*-PhCHCH_2). *trans*-Isomer: $\delta = 7.55$–6.83 (m, 16H, Ar*H* + CNC*H*), 4.59 (d, $J = 7.3$ Hz, 1H, PhC*H*CH_2), 3.48 (dd, $J = 7.4$, 18.8 Hz, 1H, *trans*-PhCHCH_2), 2.80 (dd, $J = 2.0$, 18.8 Hz, 1H, *cis*-PhCHCH_2). ^{13}C NMR ($CDCl_3$): $\delta = 177.6$, 175.9, 163.5, 143.5, 133.9, 130.9, 128.9, 128.6, 127.5, 127.4, 127.0, 126.7, 123.6, 121.0, 119.9, 48.9, 39.9. ESI-MS, *m*/*z* (%): 310.2. (100) [(M+H)$^+$]. IR (KBr) [cm^{-1}]: $\tilde{\nu} = 3061$ w, 3026 w, 1618 s, 1585 vs, 1483 s, 1445 m, 1266 m, 1203 m, 776 m, 756 s, 699 vs. Anal. calc. for $C_{23}H_{19}N$ (309.4): C, 89.28; H, 6.19; N, 4.53. Found: C, 87.88; H, 5.88; N, 4.24%.

4.2.3. N-(4-methyl)phenyl-3,4-diphenylcyclo-2-pentene imine (**2b**)

Route A reagents: 3,4-Diphenylcyclo-2-pentenone 1 (1.50 g, 6.40 mmol), 4-methylaniline (2.14 g, 20 mmol), *p*-toluenesulfonic acid (75.0 mg, 0.32 mmol), reaction time: 1 h, yield: 1.55 g (75%), pale-green powder. ^{1}H NMR ($CDCl_3$): *cis*/*trans* = 1.8/1; *cis*-isomer: = 7.52–6.90 (m, 15H, Ar*H* + CNC*H*), 4.61 ("t", 1H, PhC*H*CH_2), 3.29 (dd, $J = 7.6$, 18.4 Hz, 1H, *trans*-PhCHCH_2), 2.59 (dd, $J = 2.1$, 18.0 Hz, 1H, *cis*-PhCHCH_2), 2.30 (s, 3H, CH_3). *trans*-isomer: = 7.52-6.90 (m, 15H, Ar*H* + CNC*H*), 4.61 ("t", 1H, PhC*H*CH_2), 3.60 (dd, $J = 7.6$, 18.4 Hz, 1H, *trans*-PhCHCH_2), 2.87 (dd, $J = 2.1$, 18.0 Hz, 1H, *cis*-PhCHCH_2), 2.37 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): $\delta = 142.9$, 133.8, 133,5, 130,2, 129.8, 128.7, 128.5, 127.9, 127.8, 127.0, 126.2, 121.8, 121.4, 120.6, 49.3, 48.0, 40.6, 20.9, 15.3. ESI-MS, *m*/*z* (%): 324.5. (100) [(M+H)$^+$]. IR (KBr) [cm^{-1}]: $\tilde{\nu} = 3022$ w, 2925 w, 1621 s, 1590 vs, 1484 s, 1445 m, 1265 m, 1205 m, 776 m, 757 s, 699 s. Anal. calc. for $C_{24}H_{21}N$ (323.4): C, 89.12; H, 6.54; N, 4.33. Found: C, 88.78; H, 6.04; N, 4.17%.

4.2.4. N-mesityl-3,4-diphenylcyclo-2-pentene imine (**2c**)

Route A reagents: 3,4-Diphenylcyclo-2-pentenone 1 (2.00 g, 8.54 mmol), mesitylamine (3.40 g, 25 mmol), *p*-toluenesulfonic acid (0.11 g, 0.43 mmol), reaction time: 12 h, yield: 2.03 g (77%), green powder. *Route B reagents:* 3,4-Diphenylcyclo-2-pentenone 1 (1.17 g, 5.0 mmol), mesitylamin (4.05 g, 30.0 mmol), $TiCl_4(thf)_2$ (1.82 g, 5.45 mmol), yield: 1.02 g (58%), light green powder. ^{1}H NMR ($CDCl_3$): *cis*/*trans* = 3.5/1; *cis*-isomer (* indicates overlap with *cis*-isomer): $\delta = 7.55$–6.75 (m*, 13H, Ar*H* + CNC*H*), 4.50 (d, $J = 7.3$ Hz, 1H, PhC*H*CH_2), 2.81 (dd, $J = 7.4$, 18.8 Hz, 1H, *trans*-PhCHCH_2), 2.55 (m* 1H, *cis*-PhCHCH_2), 2.25 (s, 3 H, Ar(CH_3)), 2.10 (s, 3 H, Ar(CH_3)), 2.01 (s, 3 H, Ar(CH_3)). *trans*-Isomer (* indicates overlap with *cis*-isomer): $\delta = 7.55$–6.75 (m, 13H, Ar*H*), 6.46 (s, 1H, CNC*H*), 4.60 (d, $J = 7.3$ Hz, 1H, PhC*H*CH_2), 3.59 (dd, $J = 7.4$, 18.8 Hz, 1H, *trans*-PhCHCH_2), 2.87 (dd, $J = 1.8$, 18.8 Hz, 1H, *cis*-PhCHCH_2), 2.32 (s, 3 H, Ar(CH_3)), 2.17 (s, 3 H, Ar(CH_3)), 2.05 (s, 3H, Ar(CH_3)). ^{13}C NMR ($CDCl_3$): $\delta = 178.3$, 176.4, 174.3, 163.5, 159.0, 146.8, 145.2, 143.6, 141.7, 134.3, 133.8, 132.1, 130.3, 125.5, 125.3, 125.0, 124.8, 113.2, 93.8, 48.6, 20.7, 18.3, 17.6. ESI-MS, *m*/*z* (%): 352.5 (100) [(M+H)$^+$]. IR (KBr) [cm^{-1}]: $\tilde{\nu} = 2915$ w, 2852 w, 1643 vs, 1595 s, 1491 s, 1476 s, 1445 s, 1263 m, 1207 s, 1144 m, 1030 m, 853 s, 759 s, 699 s. Anal. calc. for

$C_{26}H_{25}N$ (351.5): C, 88.85; H, 7.17; N, 3.99. Found: C, 88.45; H, 7.30; N, 3.93%.

4.2.5. N-(2,6-diisopropyl)phenyl-3,4-diphenylcyclo-2-pentene imine (**2d**)

Route A reagents: 3,4-Diphenylcyclo-2-pentenone 1 (2.00 g, 8.54 mmol), 2,6-diisopropylaniline (4.45 g, 25 mmol), *p*-toluenesulfonic acid (0.11 g, 0.43 mmol), reaction time: 24 h, yield: 2.41 g (72%), dark green powder. *Route B reagents:* 3,4-Diphenylcyclo-2-pentenone 1 (1.17 g, 5.0 mmol), 2,6-diisopropylaniline (5.32 g, 30.0 mmol), $TiCl_4(thf)_2$ (1.82 g, 5.45 mmol), yield: 1.57 g (47%), green powder. ^{1}H NMR ($CDCl_3$): *cis*/*trans* = 4.2/1; *cis*-isomer (* indicates overlap with *cis*-isomer): δ = 7.52–7.02 (m*, 11H, Ar-*H* + CNC*H*), 4.56 (d, *J* = 7.3 Hz, 1H, PhC*H*CH_2), 3.05–2.80 (m*, 3H, C*H*(CH_3)textsubscript2 + *trans*-PhCHCH_2), 2.20 (dd, *J* = 2.0, 18.8 Hz, 1H, *cis*-PhCHCH_2), 1.34–1.10 (m*, 12H, CH(C$H_3)_2$). *trans*-isomer (* indicates overlap with *cis*-isomer): δ = 7.52–7.02 (m, 10 H, Ar*H*), 6.50 (s, 1H, CNC*H*), 4.68 (d, *J* = 7.3 Hz, 1H, PhC*H*CH_2), 3.58 (dd, *J* = 7.4, 18.8 Hz, 1H, *trans*-PhCHCH_2), 3.08 (sept, *J* = 6.9 Hz, 1H, C*H* $(CH_3)_2$), 3.05–2.80 (m*, 2H, C*H*$(CH_3)_2$ + *cis*-PhCHCH_2), 1.34–1.10 (m*, 6H, CH(C$H_3)_2$), 0.88 (d, *J* = 6.9 Hz, 6H, CH(*C*$H_3)_2$). ^{13}C NMR ($CDCl_3$): = 147.1, 143.7, 143.4, 140.2, 137.9, 137.7, 136.6, 133.9, 132.4, 131.1, 130.8, 129.9, 129.7, 129.5, 129.0, 128.9, 128.7, 128.5, 127.6, 127.4, 127.1, 126.8, 124.1, 123.8, 123.6, 123.3, 123.1, 123.0, 122.8, 122.5, 118.5, 48.6, 47.9, 43.6, 40.9, 28.1, 28.0, 27.8, 23.9, 23.8, 23.6, 23.3, 23.2, 23.1, 22.8, 22.4. ESI-MS, *m*/*z* (%): 394.6 (100) [$(M+H)^+$]. IR (KBr) [cm^{-1}]: $\tilde{\nu}$ = 2960 s, 2925 s, 2863 m, 2863 m, 1712 w, 1635 s, 1588 m, 1492 m, 1446 m, 758 s, 700 s. Anal. calc. for $C_{29}H_{31}N$ (393.6): C, 86.10; H, 7.64; N, 3.36. Found: C, 86.44; H, 7.49; N, 3.14%.

4.2.6. N-((R)-1-phenylethyl)-3,4-diphenylcyclo-2-pentene imine (**2e**)

Route A reagents: 3,4-Diphenylcyclo-2-pentenone 1 (1.00 g, 4.3 mmol), (*R*)-(+)-1-phenylethylamine (7.82 g, 64.5 mmol), *p*-toluenesulfonic acid (55.0 mg, 0.22 mmol), reaction time: 32 h, yield: 1.2 g (84%), yellow oil. ^{1}H NMR ($CDCl_3$): δ = 7.75–6.90 (m, 15H, Ar*H*), 4.85 (d, 1H, PhC*H*CH_2), 4.41 (d, 1H, *trans*-PhCHCH_2), 3,32 (d, 1H, *cis*-PhCHCH_2), 2.61 (m, 1H, NC*H*), 1.50 (m, 3H, NCHCH_3) *cis*/*trans* = >20/1. ^{13}C NMR ($CDCl_3$): δ = 133.1, 127.7, 127.3, 126.8, 126.7, 126.6, 126.5, 125.9, 125.7, 124.2, 110.2, 63.9, 62.3, 49.2, 48.8, 39.2, 25.0. ESI-MS, *m*/*z* (%): 338.4 (100) [$(M+H)^+$]. IR (KBr) [cm^{-1}]: $\tilde{\nu}$ = 1642 m,160 w, 1493 m, 1263 w, 1029 w, 757 s, 724 m, 698 s. Anal. calc. for $C_{25}H_{23}N$ (337.5): C, 88.98; H, 6.87; N, 4.15. Found: C, 88.59; H, 6.77; N, 4.17%.

4.2.7. General procedure for the synthesis of 1,1′-diamino-3,4-diphenylcyclopentadienyl iron(II) compounds **3a**–**3e**

A solution of the imine ligand (1 eq.) in THF (10 mL/mmol imine ligand) was cooled to −78 °C and LDA (2.5 eq.) was added and stirred for 1 h. Successive addition of $FeCl_2$ (0.5 eq.) led to a colour change to red brown. The reaction mixture was slowly warmed to room temperature and after the time mentioned all volatiles were removed *in vacuo*. The residue was dissolved in methanol and stirred for 5 min during which a orange solid precipitated. Different work-up procedures followed depending on the desired products.

4.2.8. Bis(1-anilino-3,4-triphenylcyclopentadienyl) iron(II) (**3a**)

Reagents: **2a** (2.8 g, 9.05 mmol), LDA (11.3 mL, 22.6 mmol), $FeCl_2$ (573 mg, 4.53 mmol), reaction time: 16 h. The crude product was filtered off, washed with cold methanol, dried *in vacuo* and re-crystallised from benzene. Yield: 1.98 g (65%), orange powder. ^{1}H NMR (C_6D_6): δ = 7.39–7.36 (m, 8H, $Ar_{Cp}H$), 7.05 (m, 4 H, Ar_NH), 7.01–6.99 (m, 12H, $Ar_{Cp}H$), 6.73 (t, *J* = 7.3 Hz, 2H, Ar_NH), 6.58 (6, *J* = 7.2 Hz, 4H, Ar_NH), 4.62 (s, 2H, N*H*), 4.39 (s, 4H, Cp-*H*). ^{13}C NMR (d_8-THF): δ = 146.5, 138.2, 130.6, 129.5, 128.4, 126.6, 119.1, 116.2, 103.0, 83.8, 67.1[#]. ESI-MS, *m*/*z* (%): 672.6 (100) [M^+]. Anal. calc. for $C_{46}H_{36}FeN_2$ (672.6): C, 82.14; H, 5.39; N, 4.16. Found: C, 81.82; H, 5.41; N, 4.14%.

Synthesis via the silylamide route: A mixture of the imine **2a** (2.5 g, 8.1 mmol) and freshly distilled $Fe[N(SiMe_3)_2]_2(thf)$ (**4**, 1.5 g, 4.0 mmol) was refluxed for 14 day while the colour changed from green to brown. Afterwards, all volatiles were removed *in vacuo* and the product was purified by inert gas column chromatography (CH_2Cl_2/EtOAc/Et_3N) 1/1/0.02. Yield: 1.74 g (62%), orange powder.

4.2.9. Bis(1-(4-methyl)anilino-3,4-triphenylcyclopentadienyl) iron(II) (**3b**)

Reagents: **2b** (2.92 g, 9.05 mmol), LDA (11.3 mL, 22.6 mmol), $FeCl_2$ (573 mg, 4.53 mmol), reaction time: 24 h. The crude product was filtered off, washed with cold methanol, dried *in vacuo* and re-crystallised from benzene. Yield: 2.03 g (64%), orange powder. ^{1}H NMR (C_6D_6): δ = 7.41–7.37 (m, 8H, $Ar_{Cp}H$), 7.02–6.99 (m, 12H, $Ar_{Cp}H$), 6.86 (t, *J* = 7.5 Hz, 4H, Ar_NH), 6.47 (d, *J* = 7.5 Hz, 4H, Ar_NH), 4.60 (s, 2H, N*H*), 4.36 (s, 4H, Cp-*H*), 2.21 (s, 6H, CH_3). ^{13}C NMR (d_8-THF): δ = 144.7, 138.1, 130.6, 130.1, 128.2, 126.5, 125.3, 116.0, 103.9, 83.6, 67.1[#], 23.1. ESI-MS, *m*/*z* (%): 700.8 (100) [M^+]. Anal. calc. for $C_{46}H_{36}FeN_2$ (700.7): C, 82.28; H, 5.75; N, 4.00. Found: C, 81.73; H, 5.31; N, 4.11%.

4.2.10. Bis(1-N-(2,4,6-trimethylphenyl)-3,4-diphenylcyclopentadienyl) iron(II) (**3c**)

Reagents: **2c** (1.0 g, 2.8 mmol), LDA (3.5 mL, 7.0 mmol), $FeCl_2$ (180 mg, 1.4 mmol), reaction time: 32 h. The crude product was purified by inert gas column chromatography (CH_2Cl_2/EtOAc/Et_3N) 1/1/0.02. Yield: 401 mg (38%), dark-orange powder. ^{1}H NMR (C_6D_6): δ = 7.43–7.40 (m, 8H, $Ar_{Cp}H$), 7.04–7.00 (m, 12H, $Ar_{Cp}H$), 6.84 (s, 2 H, Ar_NH), 4.58 (s, 2H, N*H*), 4.31 (s, 4H, Cp-*H*),

2.21 (s, 6H, Ar(CH_3)), 2.14 (s, 12H, Ar(C H_3)). ^{13}C NMR (d_8-THF): $\delta = 139.8$, 138.3, 130.4, 128.6, 128.1, 126.3, 125.9, 122.5, 103.0, 83.8, 66.5$^{\#}$, 20.5, 17.7. ESI-MS, *m/z* (%): 756.6 (100) [M^+]. Anal. calc. for $C_{52}H_{48}FeN_2$ (756.8): C, 82.53; H, 6.39; N, 3.70. Found: C, 81.98; H, 6.23; N, 3.88%.

4.2.11. Bis(1-N-(2,6-diisopropylphenyl)-3,4-diphenyl-cyclopentadienyl) iron(II) (**3d**)

Reagents: **2d** (1.01 g, 2.56 mmol), LDA (3.2 mL, 6.4 mmol), $FeCl_2$ (162 mg, 1.28 mmol), reaction time: 32 h. The crude product was purified by inert gas column chromatography with *n*-hexane/EtOAc/Et_3N (10/5/1). Yield: 350 mg (33%), brown-orange powder. ^{1}H NMR (C_6D_6): $\delta = 7.46$–7.42 (m, 8H, Ar_{Cp} *H*), 7.08–7.00 (m, 16H, Ar*H*), 6.89 (t, $J = 7.3$ Hz, 2H, Ar_N*H*), 4.43 (s, 2H, N*H*), 4.30 (s, 4H, Cp-*H*), 2.94 (sept, $J = 6.8$ Hz, 2H, C*H*(CH_3)$_2$), 1.28 (d, sept, $J = 6.8$ Hz, 12H, CH(CH_3)$_2$). ^{13}C NMR (d_8-THF): $\delta = 139.5$, 138.4, 132.7, 130.4, 128.6, 126.7, 119.8, 118.0, 113.1, 84.2, 66.1$^{\#}$, 28.2$^{\#}$, 22.5. ESI-MS, *m/z* (%), 840.7 (100) [M^+]. Anal. calc. for $C_{58}H_{60}FeN_2$ (841.0): C, 82.84; H, 7.19; N, 3.33. Found: C, 82.55; H, 6.94; N, 3.18%.

4.2.12. Bis(1-N-((R)-1′-phenylethyl)-3,4-diphenyl-cyclopentadienyl) iron(II) (**3e**)

Reagents: **2e** (1.17 g, 3.12 mmol), LDA (3.9 mL, 7.8 mmol), $FeCl_2$ (198 mg, 1.56 mmol), reaction time: 34 h. The crude product was purified by inert gas column chromatography with *n*-hexane/EtOAc/Et_3N 10/5/1. Yield: 422 mg (37%), orange-red powder. ^{1}H NMR (C_6D_6):=7.47-7.30 (m, 12 H, Ar*H*), 7.20-6.99 (m, 18H, Ar*H*), 4.27 (s, 4H, Cp-*H*), 4.10 (dd, 2H, NC*H*), 2.44 (s, 2H, N*H*), 1.24 (d, $J = 8.9$ Hz, 6H, NCHC H_3). ^{13}C NMR (d_8-THF): $\delta = 146.6$, 139.1, 130.2, 128.5, 128.3, 128.1, 126.0, 116.2, 113.7, 82.1, 66.9$^{\#}$, 56.8, 25.6$^{\#}$. ESI-MS, *m/z* (%): 728.5 (100) [M^+]. Anal. calc. for $C_{50}H_{44}FeN_2$ (728.7): C, 82.41; H, 6.09; N, 3.84. Found: C, 81.79; H, 5.89; N, 3.70%.

4.3. X-ray structural analysis of **3a**

Data were measured on a Oxford-Diffractions Xcalibur3 diffractometer with area detector using graphite-monochromated Mo Kα radiation. Intensities were measured using $\phi + \omega$ scans at 150 K. Compound **3a** crystallised in the monoclinic space group $P2_1/c$ [$a = 7.4576(4)$ Å, $b = 16.786(1)$ Å, $c = 26.805(1)$ Å; $\beta = 97.004(4)°$; $R_1 = 0.143$; $wR_2 = 0.178$]. The small crystal dimensions made a data cut off the at $\theta = 18.6°$ necessary. Due to the low data to parameter ratio all carbon atoms were refined isotropically. All hydrogen atoms were geometrically placed, and were allowed to ride on their respective atoms. The structure was solved using direct methods with SHELXS-97 [21] and the refinement (based on F^2 of all data) was performed by full matrix least-squares techniques with SHELXL-97 [22].

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Appendix A. Supplementary material

CCDC 668199 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.12.020.

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