

Heterobimetallic Fe–Pd and Fe–Pt NCN pincer complexes (NCN = [C₆H₂(CH₂NMe₂)_{2-2,6}][−])

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Abstract

The *meta*-diaminoaryl ferrocenes Fc–NCN–H (**3**) and Fc–C≡C–NCN–H (**5**) (Fc = (η⁵-C₅H₅)(η⁵-C₅H₄)Fe, NCN–H = C₆H₃(CH₂NMe₂)_{2-3,5}) can be used as precursors in the preparation of heterobimetallic transition metal complexes of structural type Fc–NCN–MX (NCN = [C₆H₂(CH₂NMe₂)_{2-2,6}][−]; MX = PdCl (**7**), PtCl (**8**), PtI (**9**)) and Fc–C≡C–NCN–MX (MX = PdCl (**11**), PdI (**12**), PtCl (**13**)), respectively. They are accessible by applying different synthesis procedures, including oxidative addition and metallation–transmetallation processes.

Cyclic voltammetric studies show that the ferrocene moieties in **3**, **5**, **7–9** and **11–13** can reversibly be oxidised. The potential of the Fe(II)/Fe(III) redox couple decreases with increasing electron density at the NCN pincer unit. The use of **8** as a possible (electro)chemical sensor in the detection of SO₂ is discussed as well.

The solid-state structures of **8** and **13** are reported. The crystals of **8** contain two molecules of **8** in the asymmetric unit. The plane of the C₆H₂ moiety is with 27.2(3)° and 38.2(3)° tilted towards the C₅H₄ entity, while in **13** an angle of 45.9(3)° can be found. The d⁸-electron configured platinum atoms possess a somewhat distorted square-planar surrounding, setup by two Me₂NCH₂ *ortho*-substituents, the NCN C_{ipso} carbon atom and the chloride ligand.

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1. Introduction

Over the last years, the manifold coordination chemistry of diphosphino- and disulfido-aryl anions and the related diaminoaryl pincers NCN (NCN = [C₆H₃(CH₂NMe₂)_{2-2,6}][−]) towards different transition metal ions has been intensively investigated [1,2]. In this accessible transition metal pincer complexes, stable metal–carbon

σ-bonds are present, due to the chelating effect of, *i.e.* the two Me₂NCH₂ *ortho*-substituents [3]. The synthesis of *para*-functionalised Y–NCN–MX complexes (M = Ni, Pd, Pt; X = halide; Y = alkynyl, halide, ...) opens the possibility to prepare larger molecules with specific physical and chemical properties [4]. Such species are of particular interest, since they can be used as building blocks in, for example, the synthesis of one-dimensional molecular wires with electronic conduction along a linear π-conjugated organometallic chain [5]. They also provide an entry into liquid crystalline materials [6], homogeneous catalysis or molecular electronics, *i.e.* optical and physical sensors [7]. Among them, redox-active organic and/or

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organometallic species with reversibly switchable electron density and electronic properties are attractive building blocks. The one-electron reservoir ferrocene is, due to its robustness, a most promising unit to be incorporated in such multimetallic assemblies.

The oxidation of ferrocene-based compounds is possible by using electrochemical methods such as cyclic voltammetry to determine the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox potential and with that the electron density at the ferrocene moiety. This gives rise to the possibility to use such systems as sensory materials which can electrochemically be read out.

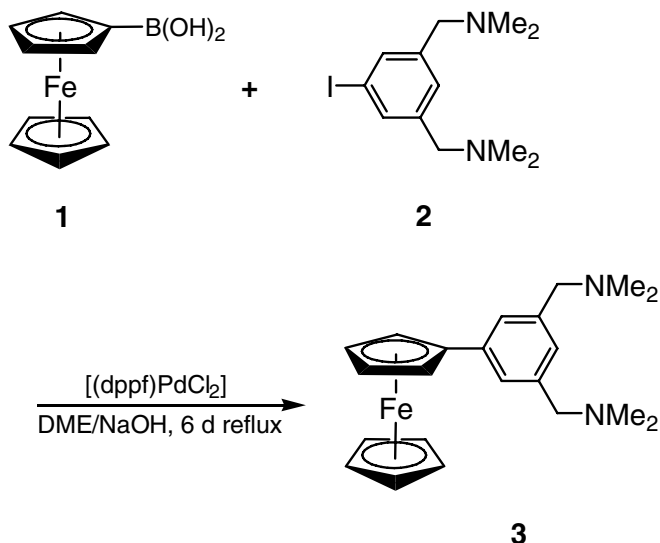
We report here on the synthesis of NCN pincer-substituted ferrocenes of type Fc-NCN-H and $\text{Fc-C}\equiv\text{C-NCN-H}$ ($\text{NCN-H} = \text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-3,5}$) and on their subsequent metallation to heterobimetallic Fc-NCN-MX and $\text{Fc-C}\equiv\text{C-NCN-MX}$ complexes ($\text{NCN} = [\text{C}_6\text{H}_2(\text{CH}_2\text{NMe}_2)_{2-2,6}]^-$; $\text{M} = \text{Pd}, \text{Pt}$; $\text{X} = \text{Cl}, \text{I}$), respectively. Their electrochemical behaviour and reversible absorption ability towards SO_2 is discussed as well.

2. Results and discussion

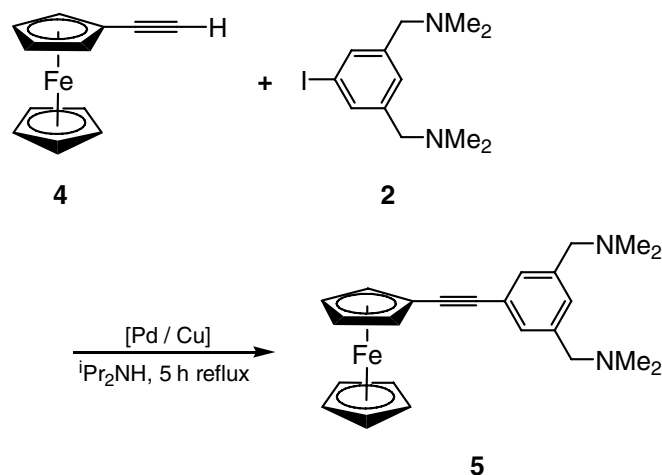
2.1. Synthesis and spectroscopy

Carbon–carbon cross-coupling catalysed by transition metals can successfully be used to prepare rigid-rod structured π -conjugated organic and organometallic NCN pincer-functionalised ferrocenes [8,9].

Treatment of Fc-B(OH)_2 (**1**) ($\text{Fc} = (\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4)\text{Fe}$) with I-1- $\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-3,5}$ (**2**) following the Suzuki cross-coupling protocol [8e] in presence of catalytic amounts of $[(\text{dppf})\text{PdCl}_2]$ ($\text{dppf} = 1,1'$ -bis(diphenylphosphino)ferrocene) gives Fc-NCN-H (**3**) ($\text{NCN-H} = \text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-3,5}$) (Eq. (1)) which after appropriate work-up, can be isolated as a red oil in 27% yield.



In **3** the NCN pincer moiety is connected to the ferrocene core *via* a single carbon–carbon bond. This might lead to repulsive interactions between the *ortho*-hydrogen atoms of the C_5H_4 and C_6H_3 rings and hence, these two planes will be twisted towards each other. This may prevent an effective electronic communication between the iron atom and the metallated NCN pincer unit. Thus, the insertion of a suitable π -conjugated $\text{-C}\equiv\text{C-}$ or -C=C- spacer is a promising alternative, although the electronically interacting parts will be more separated from each other. Therefore, $\text{Fc-C}\equiv\text{C-NCN-H}$ (**5**) was prepared in a Sonogashira reaction [8d] by reacting $\text{Fc-C}\equiv\text{CH}$ (**4**) with **2** in the presence of catalytic amounts of $[(\text{Ph}_3\text{P})_2\text{PdCl}_2]/[\text{CuI}]$ in diisopropyl amine as solvent (Eq. (2)). After appropriate work-up, **5** could be isolated as an orange-red oil in 75% yield.

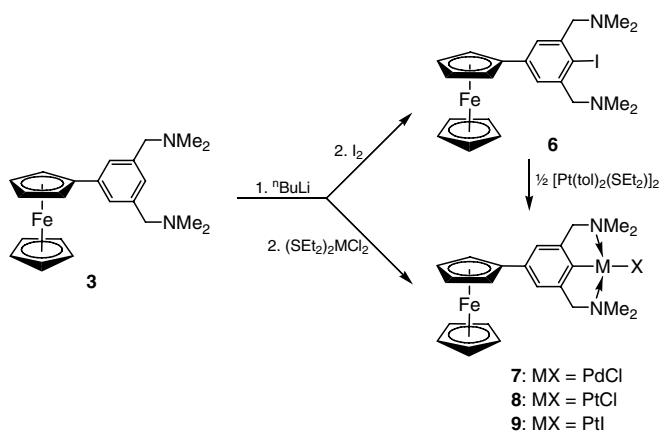


Compounds **3** and **5** are soluble in common organic solvents, such as *n*-hexane, toluene, diethyl ether and dichloromethane.

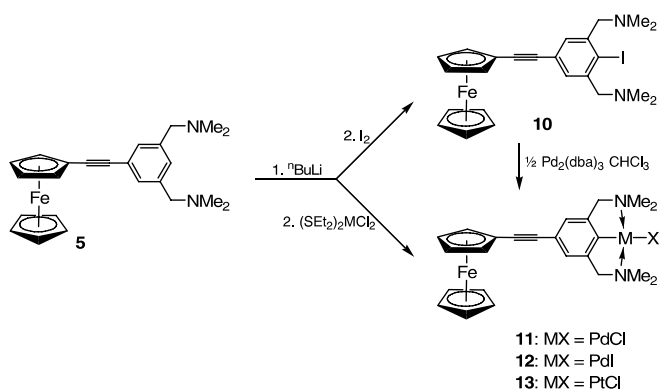
Treatment of *n*-hexane solutions containing **3** or **5** with $n\text{-BuLi}$ gave **Li-3** and **Li-5** which further react with an excess of iodine to produce the iodo-functionalised sandwich complexes Fc-NCN-I (**6**) and $\text{Fc-C}\equiv\text{C-NCN-I}$ (**10**) as orange oils in 82% and 80% yield, respectively (Schemes 1 and 2).

On reacting either **6** with equimolar amounts of $[\text{Pt}(\text{tol})_2(\text{SET}_2)_2]$ ($\text{tol} = 4\text{-tolyl}$) in refluxing toluene for 5 min, or **10** with stoichiometric amounts of the Pd source $[\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3]$ ($\text{dba} = \text{dibenzylideneacetone}$) in benzene at 25°C , an oxidative addition of the C–I bond in **6** and **10** to M ($\text{M} = \text{Pd}, \text{Pt}$) occurs. After appropriate work-up, the respective orange coloured heterobimetallic complexes Fc-NCN-PtI (**9**) and $\text{Fc-C}\equiv\text{C-NCN-PdI}$ (**12**) can be isolated in 71% and 73% yield, respectively (Schemes 1 and 2).

A possibility to synthesise **7**, **8**, **11** and **13** is given by a two-step metallation–*transmetallation* procedure: lithiation of **3** and **5** by the addition of $n\text{-BuLi}$ (vide supra) and subsequent treatment of **Li-3** and **Li-5** with $[(\text{Et}_2\text{S})_2\text{PdCl}_2]$ or



Scheme 1. Synthesis of 6–9.



Scheme 2. Synthesis of 10–13.

[(Et₂S)₂PtCl₂] in a 1:1 molar ratio produces heterobimetallic Fc–NCN–MCl (7: M = Pd; 8: M = Pt) or Fc–C≡C–NCN–MCl (11: M = Pd; 13: M = Pt) in yields between 30% and 75% (Schemes 1 and 2). Nevertheless, the presence of a C≡C triple bond as given in 11 and 13 decreases the yield of these compounds significantly. A similar trend was found for NCN pincer-functionalised ferrocenes with two C≡C moieties, where the metallation–*trans*metallation procedure failed [9,10]. In comparison, the iodine-oxidative addition route (synthesis of 12) doubles the yield (58%), when compared with the lithium-*trans*metallation protocol (11: 29%).

The ¹H NMR spectra of 3, 5, 6 and 10 show the expected resonance signals typical for *non*-metallated NCN-pincer complexes [2,3]. The Me₂N and CH₂ protons appear as singlets at 2.26 and 3.43 ppm for 3 and 2.23 and 3.37 ppm for 5. The appropriate resonances for 6 and 10 are observed at 2.35 and 3.54 ppm (6) and 2.34 and 3.51 ppm (10). Coordination of the *ortho*-Me₂NCH₂ substituents to palladium (7, 11 and 12) or platinum (8, 9 and 13) results in a significant low-field shift of the Me₂N (2.9–3.2 ppm) and CH₂ (ca. 4.0 ppm) protons. The signals for the C₆H₂ entity also confirm the binding of this group to Pd and Pt. Thus, due to the increased electron density at the benzene ring a high-field shift from 7.31 3 or 7.33 ppm 5 to, for example, 6.90 ppm for 7 and 11 is observed (Section

3). In addition, the FePt complexes 8, 9 and 13 show typical ¹⁹⁵Pt satellites with coupling constants of 36–38 Hz (³J_{PtH(Me)}) and ca. 46 Hz (³J_{PtH(CH₂)}).

In the ¹³C{¹H} NMR spectra of 7–9 and 11–13 the downfield shift of the CH₂ and NMe₂ carbon atoms upon complexation to the group-10 transition metals is observed as well (*i.e.* 3: 64.4, 45.4 ppm; 9: 76.8, 56.3 ppm). The ferrocene *ipso*-carbon atoms for 3 and 6–9, where the C₆H₂ group is directly bonded to the cyclopentadienyl ring, appears between 84 and 87 ppm. For 5 and 10–13 the presence of a C≡C spacer unit between the sandwich and the NCN pincer moieties shifts the resonance signal of this carbon atom to ca. 65 ppm.

All other resonances for the ferrocene entity in 3 and 5–13 in both the ¹H and ¹³C{¹H} NMR spectra are not significantly influenced by the differently substituted NCN units and appear in the region typical for ferrocene-based complexes.

The C≡C stretching frequencies in 5 and 10–13 are not affected by the introduction of iodine, palladium or platinum and are found at ca. 2210 cm⁻¹ in the IR spectra of these species.

2.2. Electrochemical studies

Cyclic voltammetric studies were carried out for 2, 3, 7 and 8, in acetonitrile and for 5, 8 and 11–13 in tetrahydrofuran solutions. As examples, the cyclic voltammograms of 2 and 7 are depicted in Figs. 1 and 2, respectively.

The cyclic voltammogram of 2 shows an irreversible oxidation at +0.76 V, which also has been found at similar potentials for complexes 3, 5, 7, 8 and 11–13 (Table 1). It most likely arises from the oxidation of the NCN pincer unit [9,11]. An analogous behaviour has been reported for benzyl amine [12]. The second wave at +2.13 V can be assigned to the I⁻/I₂ oxidation.

The redox potentials of monometallic 3 and 5 are, when compared to the Cp₂Fe/Cp₂Fe⁺ redox-couple (Cp₂Fe = (η⁵-C₅H₅)₂Fe), shifted to a somewhat more positive value (Table 1). This change can be explained by the presence of electron withdrawing groups (the NCN pincer and the C≡C moieties) in 3 and 5 compared to ferrocene, taken as standard [13].

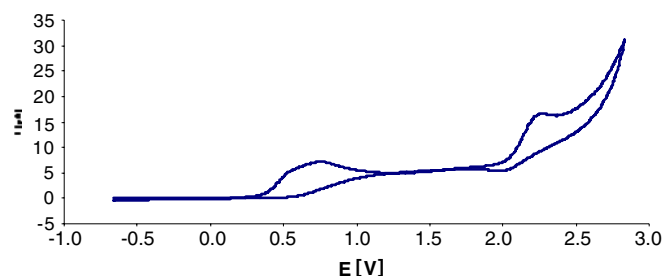


Fig. 1. Cyclic voltammogram of 2 in acetonitrile in the presence of [*n*-Bu₄N][PF₆] (*c* = 0.10 M, 25 °C, argon, scan rate = 200 mV s⁻¹). Potentials are referenced to the Cp₂Fe/Cp₂Fe⁺ redox couple as internal standard (Cp₂Fe = (η⁵-C₅H₅)₂Fe, E_{1/2} = 0.00 V).

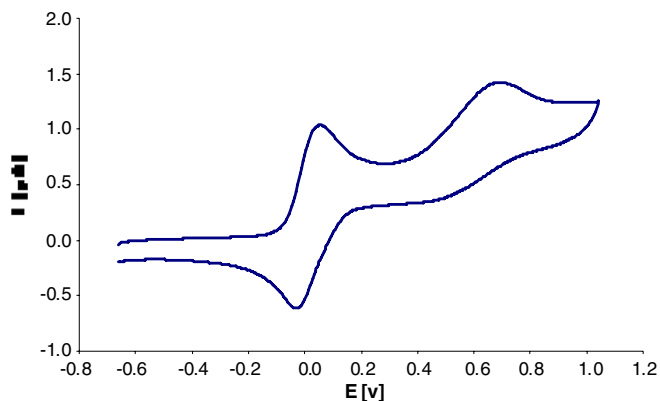


Fig. 2. Cyclic voltammogram of **7** in acetonitrile in the presence of $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ ($c = 0.10$ M, 25°C , argon, scan rate = 200 mV s^{-1}). Potentials are referenced to the $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$ redox couple as internal standard ($\text{Cp}_2\text{Fe} = (\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$, $E_{1/2} = 0.00$ V).

Table 1
Electrochemical data of **2**, **3**, **5**, **7**, **8** and **11–13**^a

Compound	$E_{1/2}$ (V)	ΔE_p (mV)	E_{ox} (V)
I–NCNH (2) ^b			+0.76, +2.13
$\text{CpFe}(\text{C}_5\text{H}_4\text{NCNH})$ (3) ^b	+0.02	80	+0.72
$\text{CpFe}(\text{C}_5\text{H}_4\text{C}_2\text{NCNH})$ (5) ^c	+0.10	192	+0.83
$\text{CpFe}(\text{C}_5\text{H}_4\text{NCNPdCl})$ (7) ^b	+0.01	85	+0.70
$\text{CpFe}(\text{C}_5\text{H}_4\text{NCNPtCl})$ (8) ^b	−0.02	70	+0.68
$\text{CpFe}(\text{C}_5\text{H}_4\text{NCNPtCl})$ (8) ^c	−0.05	146	+0.69
$\text{CpFe}(\text{C}_5\text{H}_4\text{C}_2\text{NCNPdCl})$ (11) ^c	+0.08	150	^d
$\text{CpFe}(\text{C}_5\text{H}_4\text{C}_2\text{NCNPdI})$ (12) ^c	+0.06	105	+0.76
$\text{CpFe}(\text{C}_5\text{H}_4\text{C}_2\text{NCNPtCl})$ (13) ^c	−0.03	133	+0.73

^a $E_{1/2}$ is the potential of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple, ΔE_p is the peak-to-peak separation between the reduction and oxidation wave maxima, E_{ox} is the potential of the irreversible oxidation.

^b In acetonitrile.

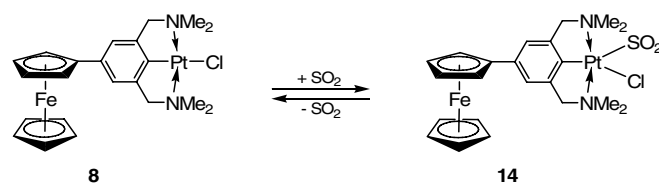
^c In tetrahydrofuran.

^d Broad oxidation wave which could not be assigned, due to the electrochemical window of the solvent used.

The NCN complexation to either palladium or platinum in **7**, **8** and **11–13** leads to a small shift of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ potentials to negative values (Table 1). For example, the cyclic voltammogram of **7** reveals the ferrocene-based wave at +0.01 V, showing a small influence of the presence of the palladium(II) ion on the redox potential of the iron atom. As compared with **3**, a somewhat more pronounced shift (−40 mV) for **8** is found, where a platinum(II) ion is present. A similar dependence of the ferrocene redox couple towards different metal ions was found for *bis*-NCN pincer-substituted ferrocenes [9]. This confirms that the $\text{Fe}(\text{II})$ ion is easier to oxidise, which is most likely caused by the *ortho*-metallation of the NCN pincer moiety (neutral *versus* anionic NCN; Pd(II), Pt(II)). For **11–13**, where the ferrocene and the pincer entities are connected by an acetylenic unit, an analogous dependence of the ferrocene redox-couple towards the presence of either Pd(II) or Pt(II) is observed (Table 1). The degree of interaction is thereof similar for aryl-ferrocenes with a slightly distorted overlap of the π -orbitals. This distortion overlap can be explained by on the one hand the repulsive interaction of the *ortho*-

hydrogen atoms and on the other hand by the extended distance between the interacting entities by the $\text{C}\equiv\text{C}$ triple bond.

The influence of the $\text{Fe}(\text{II})/\text{Fe}(\text{III})$ redox couple towards the presence of either palladium or platinum can also be used to monitor modifications in the electron density at the NCN building block by cyclic voltammetry. It is known that platinum–NCN pincer complexes possess the ability to reversibly bind SO_2 [14]. For example, colourless HO-NCN-PtCl absorbs gaseous SO_2 to form orange $\text{HO-NCN-Pt}(\text{Cl})(\text{SO}_2)$. This colour change is combined with a change of the electron density at the NCN pincer unit [14]. With this in mind, we treated a tetrahydrofuran solution containing **8** with SO_2 directly in the CV cell (Eq. (3)).



The potential for the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple for **8** is found at −0.05 V. Upon bubbling SO_2 through this solution this wave is shifted by 20 mV to −0.03 V upon formation of $\text{Fc-NCN-Pt}(\text{Cl})(\text{SO}_2)$ (**14**). Although the shift is relative small we address the change to the presence of coordinated SO_2 , since the measurements were performed directly after each other. This finding indicates that the iron centre becomes somewhat more difficult to oxidise, which can be explained by a reduced electron density at **14**, when compared with **8**, due to the $\eta^1\text{-S}$ coordination of SO_2 to platinum (*via* interaction of the filled $\text{Pt-}d_{z^2}$ orbital with the empty σ^* of SO_2). This denotes that these heterobimetallic ferrocene–platinum complexes may be used as chemical sensors for SO_2 . We are currently investigating this topic in further detail.

2.3. Solid state structures of **8** and **13**

Single crystals of **8** and **13** suitable for X-ray structure analysis could be obtained by slow evaporation of a solution of either **8** or **13** in a dichloromethane–acetone mixture (ratio 20:1) at -30°C . The molecular structures of **8** and **13** are shown in Figs. 3 and 4. Geometric details are listed in Table 2 and the experimental crystal data are summarised in Section 3.

Complexes **8** and **13** both crystallise in the monoclinic space group $\text{P2}_1/\text{c}$. The main molecular features of **8** and **13** resemble the structural data, characteristic for ferrocene and NCN pincer complexes [2,15]. The asymmetric unit of crystals of **8** contains two molecules of **8**, having similar bond distances and bond angles. Therefore, only the data for the residue depicted in Fig. 3 is discussed. As characteristic for other ferrocene complexes the Fe1-D1 and Fe1-D2 separations (D1 , D2 = centroids of the cyclopentadiene

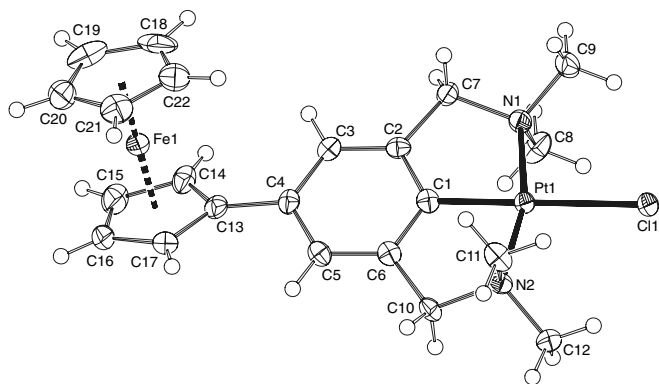


Fig. 3. Displacement ellipsoid plot of the molecular structure of **8** in the crystal, drawn at the 50% probability level. The second independent molecule is omitted for clarity.

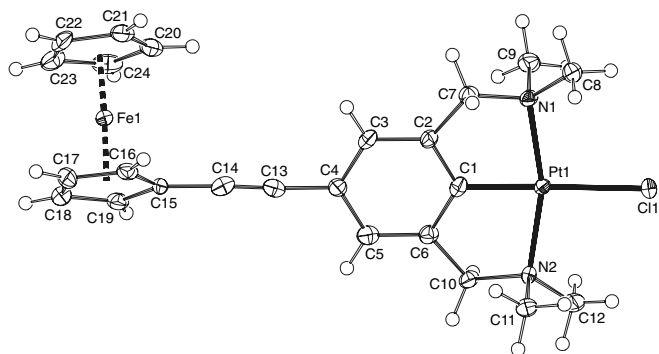


Fig. 4. Displacement ellipsoid plot of the molecular structure of **13** in the crystal, drawn at the 50% probability level.

nyl ligands C_5H_4 and C_5H_5 , respectively) are found with 1.641(2) and 1.639(3) Å for **8** and 1.634(3) Å for **13** [15]. The two cyclopentadienyl ligands are thereby rotated by $-12.2(4)^\circ$ **8** or $2.5(5)^\circ$ **13** with respect to each other, which verifies an almost eclipsed conformation. The metals Pt1 (**8** and **13**) adopt a distorted square-planar geometry set-up by

C1, N1, N2 and Cl1 (Figs. 3 and 4). The C1–Pt1–Cl1 bond angles are with $177.57(11)^\circ$ **8** and $178.91(19)^\circ$ **13** almost linear, whereas the N1–Pt1–N2 angles with $164.65(12)^\circ$ **8** and $163.09(19)^\circ$ **13** deviate from linearity. The coordination plane around Pt1 is almost coplanar with the plane of the C_6H_2 ring (**8**: 8.9° , **13**: 12.7°). As expected, the $C\equiv C$ functionality in **13** is linear with angles of $177.0(7)^\circ$ (C4–C13–C14) and $177.3(7)^\circ$ (C13–C14–C15), respectively.

A further noticeable feature of **8** and **13** is the angle of the planes between the C_6H_2 unit and the η^5 -coordinated C_5H_4 rings. For **8** tilting angles of $27.2(3)^\circ$ and $38.2(3)^\circ$ and for **13** a value of $45.9(3)^\circ$ are found. This orientation averts an optimal overlap between the π -orbitals of the cyclopentadienyl and NCN–PtCl pincer fragments [16]. However, the interplanar angle seems mainly to depend on crystal packing effects, since for **8** two different angles were found and for **13**, with less repulsive interactions between the *ortho*-hydrogen atoms of the C_5H_4 and C_6H_2 rings, due to the $C\equiv C$ spacer, a larger value has been observed.

3. Experimental part

3.1. General methods

All reactions were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. Tetrahydrofuran, diethyl ether, benzene, toluene and *n*-hexane were purified by distillation from sodium/benzophenone ketyl. iPr_2NH was dried by distillation from KOH. Infrared spectra were recorded with a Perkin–Elmer FT-IR 1000 spectrometer. NMR spectra were recorded with a Bruker Avance 250 spectrometer (1H NMR: 250.12 MHz, $^{13}C\{^1H\}$ NMR: 62.86 MHz) or with a Varian Inova 300 spectrometer (1H NMR: 300.10 MHz, $^{13}C\{^1H\}$ NMR: 75.47 MHz) in the Fourier transform mode. Chemical shifts are reported in δ units (parts per million) downfield

Table 2
Selected bond distances (Å), angles ($^\circ$), and torsion angles ($^\circ$) for **8** and **13**^a

Bond distances		Bond angles		Torsion angles	
<i>Complex 8</i> ^c					
Pt1–Cl1	2.4452(9)	Cl1–Pt1–C1	177.57(11)	C1–C2–C7–N1	20.9(5)
Pt1–C1	1.925(4)	N1–Pt1–N2	164.65(12)	C1–C6–C10–N2	22.4(5)
Pt1–N1	2.092(3)	Cl1–Pt1–N1	96.19(9)	Pt1–N1–C7–C2	–25.6(4)
Pt1–N2	2.092(3)	Cl1–Pt1–N2	99.15(9)	Pt1–N2–C10–C6	–27.8(4)
D1–Fe1 ^b	1.641(2)	D1–Fe1–D2 ^b	178.77(15)		
D2–Fe1 ^b	1.639(3)				
<i>Complex 13</i>					
Pt1–Cl1	2.4304(15)	Cl1–Pt1–C1	178.91(19)	C1–C2–C7–N1	25.0(7)
Pt1–C1	1.914(6)	N1–Pt1–N2	163.09(19)	C1–C6–C10–N2	23.8(7)
Pt1–N1	2.102(5)	Cl1–Pt1–N1	99.43(14)	Pt1–N1–C7–C2	–32.4(5)
Pt1–N2	2.091(5)	Cl1–Pt1–N2	97.46(14)	Pt1–N2–C10–C6	–32.6(6)
C13–C14	1.169(9)	C4–C13–C14	177.0(7)		
Fe1–D1 ^b	1.634(3)	C13–C14–C15	177.3(7)		
Fe1–D2 ^b	1.634(3)	D1–Fe1–D2 ^b	177.75(17)		

^a Standard uncertainties are given in the last significant figure(s) in parenthesis.

^b D1, D2: centroids of the cyclopentadienyl ligands.

^c Only one of the two independent molecules is considered.

from tetramethylsilane ($\delta = 0.00$ ppm) with the solvent as the reference signal (CDCl_3 : ^1H NMR, $\delta = 7.26$; $^{13}\text{C}\{^1\text{H}\}$ NMR, $\delta = 77.0$). Cyclic voltammograms were recorded in a dried cell purged with purified nitrogen at 25°C . Platinum wires served as working and as counter electrode. A Ag/AgCl or a saturated calomel electrode served as reference electrode. For ease of comparison, all electrode potentials are converted using the redox potential of the ferrocene–ferrocenium couple $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$ ($\text{Cp}_2\text{Fe} = (\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$) as the reference ($E_{1/2} = 0.00$ V) [17]. Electrolyte solutions were prepared from freshly distilled acetonitrile or tetrahydrofuran and $[n\text{-Bu}_4\text{N}]\text{PF}_6$ (dried in *oil-pump vacuum* at 120°C , $c = 0.1$ M). The appropriate organometallic compounds were added at $c = 1.0$ mM. The cyclic voltammograms were recorded at a scan rate of 200 mV s^{-1} using a Princeton Applied Research EG&G 263A Analyser or a Radiometer Copenhagen DEA 101 Digital Electrochemical Analyser with an IMT 102 electrochemical interface. Melting points were determined using sealed nitrogen purged capillaries on a Gallenkamp MFB 595010 M melting point apparatus. Microanalyses were performed by the Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a. d. Ruhr and by the Department of Organic Chemistry at Chemnitz, Technical University.

3.2. General remarks

Fc-B(OH)_2 (**1**) [18], $\text{I-1-C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-3,5}$ (**2**) [19], $\text{Fc-C}\equiv\text{CH}$ (**4**) [20], $[\text{PdCl}_2(\text{SEt}_2)_2]$ [21], $[\text{PtCl}_2(\text{SEt}_2)_2]$ [21,22], $[\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3]$ [23], and $[\text{Pt}(4\text{-tol})_2(\text{SEt}_2)_2]$ [24] were prepared the following published procedures. All other chemicals were commercially available and were used as received.

3.3. Synthesis of 3

Compound **1** (1.60 g, 6.96 mmol) and 2.22 g (6.96 mmol) of **2** were dissolved in 50 mL of dimethoxymethane and 15 mL of 3 M NaOH were added. Afterward 50 mg (0.07 mmol, 1.0 mol%) of $[(\text{dppf})\text{PdCl}_2]$ were added at 25°C . After keeping the reaction mixture for 6 days at reflux it was cooled to 25°C , dissolved in 100 mL of chloroform followed by addition of 100 mL of water. The aqueous phase was extracted three times with 100 mL of diethyl ether. The combined organic phases were dried over MgSO_4 , filtered and then all volatiles were evaporated from the filtrate (*oil-pump vacuum*). Chromatography on neutral alumina (5×15 cm) with diethyl ether gave 120 mg (0.65 mmol, 9% based on **1**) of recovered Fc-B(OH)_2 . By changing the solvent to diethyl ether–tetrahydrofuran (ratio 1:2) **3** has been obtained as a red oil. Yield: 710 mg (1.89 mmol, 27% based on **1**).

^1H NMR (CDCl_3): $[\delta]$ 2.26 (s, 12H, NMe_2), 3.43 (s, 4H, CH_2N), 4.02 (s, 5H, C_5H_5), 4.29 (pt, $J_{\text{HH}} = 1.8$ Hz, 2H, C_5H_4), 4.67 (pt, $J_{\text{HH}} = 1.8$ Hz, 2H, C_5H_4), 7.07 (s, 1H, C_6H_3), 7.31 (s, 2H, C_6H_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $[\delta]$ 45.4 (NCH_3), 64.4 (NCH_2), 66.6 ($\text{CH}/\text{C}_5\text{H}_4$), 68.8 ($\text{CH}/$

C_5H_4), 69.5 ($\text{CH}/\text{C}_5\text{H}_5$), 85.3 ($^i\text{C}/\text{C}_5\text{H}_4$), 125.6 ($\text{CH}/\text{C}_6\text{H}_3$), 127.7 ($\text{CH}/\text{C}_6\text{H}_3$), 138.7 ($^i\text{C}/\text{C}_6\text{H}_3$), 139.0 ($^i\text{C}/\text{C}_6\text{H}_3$). Anal. Calc. for $\text{C}_{22}\text{H}_{28}\text{FeN}_2$ (376.31): C, 70.18; H, 7.50; N, 7.45. Found: C, 69.69; H, 7.57; N, 7.53%.

3.4. Synthesis of 5

Compound **4** (294 mg, 1.4 mmol), 318 mg (1.0 mmol) of **2**, 35 mg (0.05 mmol, 5.0 mol%) of $[(\text{Ph}_3\text{P})_2\text{PdCl}_2]$ and 10 mg (0.05 mmol, 5.0 mol%) of $[\text{CuI}]$ were dissolved in 20 mL of $^i\text{Pr}_2\text{NH}$. The reaction mixture was heated for 5 h to reflux and was then evaporated in *oil-pump vacuum*. Chromatography on neutral alumina (5×15 cm) with diethyl ether yielded 20 mg (0.10 mmol, 7% based on **2**) of recovered **4**. By changing the solvent to tetrahydrofuran compound **5** could be isolated as orange-red oil. Yield: 300 mg (0.75 mmol, 75% based on **2**).

IR (NaCl): $[\text{cm}^{-1}]$ 2212 (s) [$\nu_{\text{C}\equiv\text{C}}$]. ^1H NMR (CDCl_3): $[\delta]$ 2.23 (s, 12H, NMe_2), 3.37 (s, 4H, CH_2N), 4.20 (pt, $J_{\text{HH}} = 1.5$ Hz, 2H, C_5H_4), 4.21 (s, 5H, C_5H_5), 4.45 (pt, $J_{\text{HH}} = 1.5$ Hz, 2H, C_5H_4), 7.18 (s, 1H, C_6H_3), 7.33 (s, 2H, C_6H_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $[\delta]$ 45.3 (NCH_3), 63.9 (NCH_2), 65.3 ($^i\text{C}/\text{C}_5\text{H}_4$), 68.7 ($\text{CH}/\text{C}_5\text{H}_4$), 69.9 ($\text{CH}/\text{C}_5\text{H}_5$), 71.3 ($\text{CH}/\text{C}_5\text{H}_4$), 85.7 ($\text{FcC}\equiv\text{C}$), 88.1 ($\text{FcC}\equiv\text{C}$), 123.8 ($^i\text{C}/\text{C}_6\text{H}_3$), 129.1 ($\text{CH}/\text{C}_6\text{H}_3$), 130.7 ($\text{CH}/\text{C}_6\text{H}_3$), 138.9 ($^i\text{C}/\text{C}_6\text{H}_3$). Anal. Calc. for $\text{C}_{24}\text{H}_{28}\text{FeN}_2$ (400.33): C, 72.00; H, 7.05; N, 7.00. Found: C, 71.84; H, 6.92; N, 6.90%.

3.5. Synthesis of 6

Complex **3** (160 mg, 0.43 mmol) was dissolved in 30 mL of *n*-hexane and 0.35 mL (0.56 mmol, 1.6 M solution in *n*-hexane) of $^n\text{BuLi}$ were added at 25°C . After stirring the reaction mixture for 16 h at this temperature all volatiles were removed (*oil-pump vacuum*). The orange residue was dissolved in 30 mL of diethyl ether, treated with 200 mg (0.79 mmol) of I_2 and stirred for 6 h at 25°C . A solution of 1.0 g $\text{Na}_2\text{S}_2\text{O}_3$ in 50 mL of water was then added. The organic phase was separated, extracted with 50 mL of water, dried over MgSO_4 , filtered and evaporated in *oil-pump vacuum* to give 175 mg (0.35 mmol, 82% based on **3**) of **6** as an orange oil.

^1H NMR (CDCl_3): $[\delta]$ 2.35 (s, 12H, NMe_2), 3.54 (s, 4H, CH_2N), 4.03 (s, 5H, C_5H_5), 4.32 (pt, $J_{\text{HH}} = 1.8$ Hz, 2H, C_5H_4), 4.71 (pt, $J_{\text{HH}} = 1.8$ Hz, 2H, C_5H_4), 7.40 (s, 2H, C_6H_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $[\delta]$ 45.5 (NCH_3), 66.6 ($\text{CH}/\text{C}_5\text{H}_4$), 69.0 (NCH_2), 69.0 ($\text{CH}/\text{C}_5\text{H}_4$), 69.5 ($\text{CH}/\text{C}_5\text{H}_5$), 84.1 ($^i\text{C}/\text{C}_5\text{H}_4$), 103.9 ($^i\text{C}/\text{C}_6\text{H}_2$), 126.6 ($\text{CH}/\text{C}_6\text{H}_2$), 138.7 ($^i\text{C}/\text{C}_6\text{H}_2$), 141.5 ($^i\text{C}/\text{C}_6\text{H}_2$). Anal. Calc. for $\text{C}_{22}\text{H}_{27}\text{FeIN}_2$ (502.21): C, 52.61; H, 5.42; N, 5.58. Found: C, 52.01; H, 5.29; N, 5.76%.

3.6. Synthesis of 7

Complex **3** (100 mg, 0.28 mmol) was dissolved in 30 mL of *n*-hexane and 0.18 mL (0.28 mmol, 1.6 M solution in *n*-hexane) of $^n\text{BuLi}$ were drop-wise added at 25°C . After-

wards, the reaction mixture was stirred for 18 h at this temperature and then all volatiles were removed (*oil-pump vacuum*). The orange residue was dissolved in 30 mL of diethyl ether, treated with 100 mg (0.28 mmol) of $[(Et_2S)_2PdCl_2]$ and stirred for 18 h at room temperature. During this time a precipitate formed which was collected and dried in *oil-pump vacuum*. The orange solid was dissolved in 30 mL of dichloromethane, filtered through a pad of Celite and dried (*oil-pump vacuum*) to gave 110 mg (0.21 mmol, 76% based on $[(Et_2S)_2PdCl_2]$ of **7** as an orange solid.

M.p.: [°C] 93 (dec.). 1H NMR ($CDCl_3$): [δ] 2.97 (s, 12H, NMe_2), 4.02 (s, 4H, CH_2N), 4.04 (s, 5H, C_5H_5), 4.26 (pt, $J_{HH} = 1.8$ Hz, 2H, C_5H_4), 4.50 (pt, $J_{HH} = 1.8$ Hz, 2H, C_5H_4), 6.90 (s, 2H, C_6H_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): [δ] 53.1 (NCH_3), 66.2 (CH/C_5H_4), 68.6 (CH/C_5H_4), 69.5 (CH/C_5H_5), 74.7 (NCH_2), 86.4 ($^iC/C_5H_4$), 117.7 (CH/C_6H_2), 135.7 ($^iC/C_6H_2$), 144.9 ($^iC/C_6H_2$), 154.2 ($^iC/C_6H_2$). Anal. Calc. for $C_{22}H_{27}ClFeN_2Pd$ (517.18): C, 51.09; H, 5.26; N, 5.42. Found: C, 51.19; H, 5.26; N, 5.82%.

3.7. Synthesis of **8**

Complex **3** (110 mg, 0.29 mmol) was dissolved in 20 mL of *n*-hexane and 0.19 mL (0.30 mmol, 1.6 M solution in *n*-hexane) of nBuLi were drop-wise added at 25 °C. The reaction mixture was stirred for 18 h at room temperature. Afterward, all volatiles were removed in *oil-pump vacuum*. The orange residue was dissolved in 20 mL of diethyl ether, treated with 130 mg (0.29 mmol) of $[(Et_2S)_2PtCl_2]$ and stirred for 5 h at 25 °C. During this time a precipitate formed which was collected and dried (*oil-pump vacuum*). The orange solid was dissolved in dichloromethane, filtered through a pad of Celite and dried in *oil-pump vacuum* to gave 130 mg (0.21 mmol, 74% based on $[(Et_2S)_2PtCl_2]$ of **8** as an orange solid.

M.p.: [°C] 95 (dec.). 1H NMR ($CDCl_3$): [δ] 3.11 (s, $^3J_{PtH} = 38.4$ Hz, 12H, NMe_2), 4.05 (s, $^3J_{PtH} = 46.6$ Hz, 4H, CH_2N), 4.05 (s, 5H, C_5H_5), 4.25 (pt, $J_{HH} = 1.8$ Hz, 2H, C_5H_4), 4.51 (pt, $J_{HH} = 1.8$ Hz, 2H, C_5H_4), 6.94 (s, 2H, C_6H_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): [δ] 54.4 (NCH_3), 66.0 (CH/C_5H_4), 68.3 (CH/C_5H_4), 69.4 (CH/C_5H_5), 77.7 (NCH_2), 87.5 ($^iC/C_5H_4$), 117.4 (CH/C_6H_2), 134.1 ($^iC/C_6H_2$), 143.1 ($^iC/C_6H_2$), 143.2 ($^iC/C_6H_3$). Anal. Calc. for $C_{22}H_{27}ClFeN_2Pt$ (605.84): C, 43.61; H, 4.46; N, 4.62. Found: C, 43.81; H, 4.58; N, 4.53%.

3.8. Synthesis of **9**

Compound **6** (100 mg, 0.20 mmol) and 90 mg (0.10 mmol) of $[Pt(tol)_2(SEt_2)]_2$ were dissolved in 20 mL of toluene and were heated to reflux for 5 min. The obtained orange solution was then cooled to 25 °C and concentrated in *oil-pump vacuum* to 5 mL. Upon addition of 20 mL of *n*-hexane an orange precipitate formed which was collected, washed twice with 10 mL of hexane and 10 mL of diethyl ether and dried in *oil-pump vacuum*. Yield: 95 mg (0.14 mmol, 71% based on $[Pt(tol)_2(SEt_2)]_2$).

M.p.: [°C] 92 (dec.). 1H NMR ($CDCl_3$): [δ] 3.20 (s, $^3J_{PtH} = 38.9$ Hz, 12H, NMe_2), 4.03 (s, $^3J_{PtH} = 46.4$ Hz, 4H, CH_2N), 4.03 (s, 5H, C_5H_5), 4.25 (pt, $J_{HH} = 1.7$ Hz, 2H, C_5H_4), 4.52 (pt, $J_{HH} = 1.7$ Hz, 2H, C_5H_4), 6.93 (s, 2H, C_6H_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): [δ] 56.3 (NCH_3), 66.0 (CH/C_5H_4), 68.4 (CH/C_5H_4), 69.4 (CH/C_5H_5), 76.8 (NCH_2), 87.1 ($^iC/C_5H_4$), 117.3 (CH/C_6H_2), 134.4 ($^iC/C_6H_2$), 143.4 ($^iC/C_6H_3$), 147.5 ($^iC/C_6H_2$). Anal. Calc. for $C_{22}H_{27}FeIN_2Pt$ (697.29): C, 37.89; H, 3.90; N, 4.02. Found: C, 36.81; H, 4.58; N, 4.53%.

3.9. Synthesis of **10**

Complex **10** was prepared according to the procedure described for **6** by using 62 mg (0.15 mmol) of **5**, 0.15 mL (0.24 mmol, 1.6 M in *n*-hexane) of nBuLi and 70 mg (0.28 mmol) of I_2 . Yield: 65 mg (0.12 mmol, 80% based on **5**).

IR (NaCl): [cm^{-1}] 2211 (s) [$\nu_{C\equiv C}$]. 1H NMR ($CDCl_3$): [δ] 2.34 (s, 12H, NMe_2), 3.51 (s, 4H, CH_2N), 4.23 (bs, 7H, C_5H_4 , C_5H_5), 4.48 (pt, $J_{HH} = 1.8$ Hz, 2H, C_5H_4), 7.40 (s, 2H, C_6H_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): [δ] 45.6 (NCH_3), 65.1 ($^iC/C_5H_4$), 68.8 (NCH_2), 68.8 (CH/C_5H_4), 69.9 (CH/C_5H_5), 71.3 (CH/C_5H_4), 85.1 ($FeC\equiv C$), 89.4 ($FeC\equiv C$), 106.3 ($^iC/C_6H_2$), 123.5 ($^iC/C_6H_2$), 131.3 (CH/C_6H_2), 141.9 ($^iC/C_6H_2$). Anal. Calc. for $C_{24}H_{27}FeIN_2$ (526.23): C, 54.78; H, 5.17; N, 5.32. Found: C, 57.30; H, 6.57; N, 3.34%.

3.10. Synthesis of **11**

Heterobimetallic **11** was prepared according to the procedure described for **7**. In this respect, 100 mg (0.25 mmol) of **5**, 0.15 mL (0.38 mmol, 2.5 M in *n*-hexane) of nBuLi and 90 mg (0.25 mmol) of $[(Et_2S)_2PdCl_2]$ were reacted. Yield: 40 mg (0.07 mmol, 29% based on **5**).

M.p.: [°C] 102 (dec.). (KBr): [cm^{-1}] 2211 (w) [$\nu_{C\equiv C}$]. 1H NMR ($CDCl_3$): [δ] 2.92 (s, 12H, NMe_2), 3.96 (s, 4H, CH_2N), 4.20 (s, 5H, C_5H_5), 4.22 (pt, $J_{HH} = 1.8$ Hz, 2H, C_5H_4), 4.44 (pt, $J_{HH} = 1.8$ Hz, 2H, C_5H_4), 6.90 (s, 2H, C_6H_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): [δ] 53.0 (NCH_3), 66.2 (CH/C_5H_4), 68.7 (CH/C_5H_4), 69.8 (CH/C_5H_5), 74.7 (NCH_2), 86.4 ($^iC/C_5H_4$), 122.6 (CH/C_6H_2), 135.7 ($^iC/C_6H_2$), 144.9 ($^iC/C_6H_2$), 154.2 ($^iC/C_6H_2$). Anal. Calc. for $C_{24}H_{27}ClFeN_2Pd$ (541.20): C, 53.26; H, 5.03; N, 5.18. Found: C, 53.38; H, 5.28; N, 5.67%.

3.11. Synthesis of **12**

Complex **10** (50 mg, 0.095 mmol) and 45 mg (0.043 mmol) of $[Pd_2(dba)_3 \cdot CHCl_3]$ were dissolved in 15 mL of benzene. This reaction mixture was stirred for 18 h at 25 °C. Afterwards, 20 mL of tetrahydrofuran were added and stirring was continued for 2 h. All volatiles were evaporated in *oil-pump vacuum* and the residual greenish-black solid was dissolved in 20 mL of chloroform. The solution was filtered through a pad of Celite and concen-

trated in *oil-pump vacuum* to 2 mL. *n*-Hexane (50 mL) was added, whereby an orange solid precipitated. This precipitate was collected and washed several times with 10 mL of *n*-hexane and 10 mL of diethyl ether to gave **12** as an orange solid. Yield: 40 mg (0.063 mmol, 73% based on $[\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3]$).

M.p.: [°C] 106 (dec.). IR (KBr): $[\text{cm}^{-1}]$ 2210 (w) $[\nu_{\text{C}=\text{C}}]$. ^1H NMR (CDCl_3): $[\delta]$ 3.02 (s, 12H, NMe_2), 3.96 (s, 4H, CH_2N), 4.22 (bs, 2H, C_5H_4), 4.22 (bs, 5H, C_5H_5), 4.46 (pt, $J_{\text{HH}} = 1.8$ Hz, 2H, C_5H_4), 6.92 (s, 2H, C_6H_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $[\delta]$ 54.9 (NCH_3), 65.4 ($^i\text{C}/\text{C}_5\text{H}_4$), 68.8 ($\text{CH}/\text{C}_5\text{H}_4$), 69.9 ($\text{CH}/\text{C}_5\text{H}_5$), 71.3 ($\text{CH}/\text{C}_5\text{H}_4$), 77.3 (NCH_2), 73.8 ($\text{FcC}\equiv\text{C}$), 86.0 ($\text{FcC}\equiv\text{C}$), 120.0 ($^i\text{C}/\text{C}_6\text{H}_2$), 122.7 ($\text{CH}/\text{C}_6\text{H}_2$), 128.3 ($^i\text{C}/\text{C}_6\text{H}_2$), 145.2 ($^i\text{C}/\text{C}_6\text{H}_2$). Anal. Calc. for $\text{C}_{24}\text{H}_{27}\text{IFeN}_2\text{Pd}$ (632.65): C, 45.56; H, 4.30; N, 4.43. Found: C, 45.71; H, 4.38; N, 4.41%.

3.12. Synthesis of **13**

Compound **13** was prepared according to the procedure described for **8** by using 100 mg (0.25 mmol) of **5**, 0.16 mL (0.26 mmol, 1.6 M in *n*-hexane) of $^n\text{BuLi}$ and 100 mg (0.22 mmol) of $[(\text{Et}_2\text{S})_2\text{PtCl}_2]$. Yield: 75 mg (0.12 mmol, 53% based on **5**).

M.p.: [°C] 105 (dec.). IR (KBr): $[\text{cm}^{-1}]$ 2206 (w) $[\nu_{\text{C}=\text{C}}]$. ^1H NMR (CDCl_3): $[\delta]$ 3.08 (s, $^3J_{\text{PtH}} = 36.9$ Hz, 12H, NMe_2), 4.00 (s, $^3J_{\text{PtH}} = 46.5$ Hz, 4H, CH_2N), 4.21 (pt, $J_{\text{HH}} = 1.8$ Hz, 2H, C_5H_4), 4.22 (s, 5H, C_5H_5), 4.46 (pt, $J_{\text{HH}} = 1.8$ Hz, 2H, C_5H_4), 6.96 (s, 2H, C_6H_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $[\delta]$ 45.3 (NCH_3), 63.9 (NCH_2), 65.3 ($^i\text{C}/\text{C}_5\text{H}_4$), 68.7 ($\text{CH}/\text{C}_5\text{H}_4$), 69.9 ($\text{CH}/\text{C}_5\text{H}_5$), 71.3 ($\text{CH}/\text{C}_5\text{H}_4$), 85.7 ($\text{FcC}\equiv\text{C}$), 88.1 ($\text{FcC}\equiv\text{C}$), 123.8 ($^i\text{C}/\text{C}_6\text{H}_3$), 129.1 ($\text{CH}/\text{C}_6\text{H}_3$), 130.7 ($\text{CH}/\text{C}_6\text{H}_3$), 138.9 ($^i\text{C}/\text{C}_6\text{H}_3$). Anal. Calc. for $\text{C}_{24}\text{H}_{27}\text{ClFeN}_2\text{Pt}$ (629.86): C, 45.76; H, 4.32; N, 4.45. Found: C, 45.71; H, 4.38; N, 4.41%.

3.13. X-ray crystal structure determinations

X-ray intensities up to a resolution of $(\sin\theta/\lambda)_{\text{max}} = 0.65 \text{ \AA}^{-1}$ were measured on a Nonius Kappa CCD diffractometer with a rotating anode and a graphite monochromator ($\lambda = 0.71073 \text{ \AA}$) at a temperature of 150(2) K. The structures were solved with automated Patterson methods [25] and refined with SHELXL-97 [26] on F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were introduced in geometrically idealised positions and refined with a riding model. Geometry calculations, drawings and checking for higher symmetry were performed with the PLATON package [27].

3.14. Compound **8**

$\text{C}_{22}\text{H}_{27}\text{ClFeN}_2\text{Pt}$, $F_w = 605.85$, yellow needle, $0.42 \times 0.15 \times 0.06 \text{ mm}^3$, monoclinic, $P2_1/c$ (no. 14), $a = 14.9051$ (1), $b = 16.9068$ (2), $c = 21.5612$ (2) \AA , $\beta = 129.6807$ (4)°,

$V = 4181.60$ (9) \AA^3 , $Z = 8$, $D_x = 1.925 \text{ g cm}^{-3}$. 65 541 Reflections were measured. An analytical absorption correction was applied (PLATON [28], routine ABST, $\mu = 7.51 \text{ mm}^{-1}$, 0.14–0.78 correction range). Nine thousand five hundred and thirty-three reflections were unique ($R_{\text{int}} = 0.059$). One cyclopentadienyl ring was refined with a disorder model using split positions. 540 Parameters were refined with 154 restraints. R_1/wR_2 [$I \geq 2\sigma(I)$]: 0.0260/0.0583. R_1/wR_2 [all reflection]: 0.0398/0.0631. $S = 1.062$. Residual electron density between -1.38 and 1.40 e/\AA^3 .

3.15. Compound **13**

$\text{C}_{24}\text{H}_{27}\text{ClFeN}_2\text{Pt}$, $F_w = 629.87$, red needle, $0.42 \times 0.18 \times 0.04 \text{ mm}^3$, monoclinic, $P2_1/c$ (no. 14), $a = 12.223$ (3), $b = 15.568$ (2), $c = 11.9352$ (12) \AA , $\beta = 107.610$ (11)°, $V = 2164.7$ (7) \AA^3 , $Z = 4$, $D_x = 1.933 \text{ g cm}^{-3}$. 22713 Reflections were measured. An analytical absorption correction was applied (PLATON [28], routine ABST, $\mu = 7.26 \text{ mm}^{-1}$, 0.34–0.85 correction range). 4943 Reflections were unique ($R_{\text{int}} = 0.06$). The crystal appeared to be non-merohedrally twinned with a twofold rotation about the a -axis as twin operation. This twin relationship was taken into account during intensity evaluation [28], data reduction and refinement as HKLF5 twin [29]. 267 Parameters were refined with no restraints. R_1/wR_2 [$I \geq 2\sigma(I)$]: 0.0362/0.0904. R_1/wR_2 [all reflection]: 0.0462/0.0962. $S = 1.073$. Residual electron density between -2.51 and 2.20 e/\AA^3 .

4. Supplementary material

CCDC 284746 (complex **8**) and 284747 (**13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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