

Trimetallic FePd₂ and FePt₂ 4-ferrocenyl-NCN pincer complexes

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Abstract

Ferrocene-bridged NCN pincer complexes of structural type $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-4-NCN-1-MX})_2$ (X = I: **6**, M = Pd; **7**, M = Pt; X = Cl: **8**, M = Pt; NCN = $[\text{4-C}_6\text{H}_2(\text{CH}_2\text{NMe}_2)_2\text{-2,6}]^-$) are accessible by the subsequent reaction of $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-4-NCNH})_2$ (**4**) with ^tBuLi and $[\text{PtCl}_2(\text{SEt}_2)_2]$ (synthesis of **8**) or treatment of $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-4-NCN-1-I})_2$ (**5**) with $[\text{Pd}_2(\text{dba})_3]$ (synthesis of **6**) or $[\text{Pt}(\text{tol})_2(\text{SEt}_2)_2]$ (synthesis of **7**) (dba = dibenzylidene acetone, tol = 4-tolyl). In addition, the Sonogashira cross-coupling of $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{I})_2$ (**1**) with $\text{HC}\equiv\text{C-4-NCNH}$ (**2**) gives $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-C}\equiv\text{C-4-NCNH})_2$ (**3**). The reaction behavior of **3** towards ^tBuLi is reported as well.

Cyclovoltammetric studies show that the ferrocene entity can be oxidized reversibly. The Fe(II)/Fe(III) potential decreases with increasing electron density at the NCN pincer units due to the presence of the M-halide moiety (M = Pd, Pt).

The solid state structure of $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-4-NCN-1-PdI})_2$ (**6**) is presented. In **6** the $\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2$ unit connects two NCN-PdI pincer entities with palladium in a square-planar environment. The cyclopentadienyl ligands show a staggered conformation. The C₆H₂ rings are tilted by 23.5(3)° towards the C₅H₄ entities and the C₆H₂ plane is almost coplanar with the PdN₂^{ipso}CI coordination plane (10.3(3)°). © 2006 Elsevier B.V. All rights reserved.

Keywords: NCN Pincer; Ferrocene; Palladium; Platinum; Cyclic voltammetry; Solid state structure

1. Introduction

Recently, the synthesis and reaction chemistry of multimetallic transition metal complexes in which different metals are connected by inorganic and/or organic π -conjugated bridging units have been reported [1–6]. Such species are of special interest, due to their potential use as, for example, one-dimensional molecular wires [6]. Moreover, they are promising candidates to be used as catalysts or as optical and physical sensors. Among them, transition metal complexes featuring redox-active metals are most attractive, because both their electron density and electronic properties are easily switchable. Ferrocene is a most promising candidate to be incorporated in such multimetallic assem-

blies, since it can act as an one-electron reservoir and at the same time is a very robust compound [4,5].

Recently, the synthesis and reaction chemistry of 1,1'-bis-NCN pincer-functionalized ferrocenes of general type $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-4-NCN-1-X})_2$ (NCN = $[\text{C}_6\text{H}_2(\text{CH}_2\text{NMe}_2)_2\text{-2,6}]^-$; X = H, PdCl) were preliminary reported [4,5]. We here report on the preparation, structural features and electrochemical behavior of trimetallic FePd₂ and FePt₂ complexes of type $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-4-NCN-1-MX})_2$ (MX = PdI, PtCl, PtI).

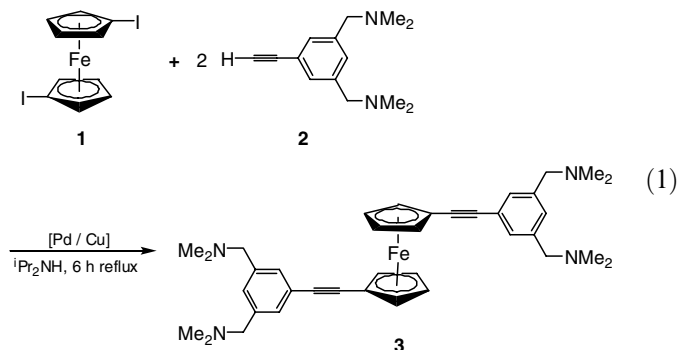
2. Results and discussion

2.1. Synthesis and spectroscopy

Palladium-catalyzed cross-coupling is an efficient synthetic method to prepare organic and organometallic compounds with π -conjugated bridging units [7]. In this

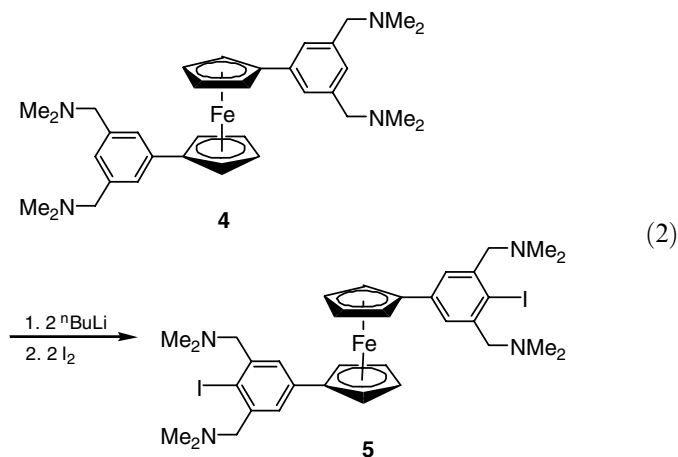
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respect, the synthesis of the 1,1'-bis-NCNH pincer-functionalized ferrocenes $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{C}\equiv\text{C-NCNH})_2$ (**3**) and $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-NCNH})_2$ (**4**) (NCNH = 1-C₆H₃(CH₂NMe₂)₂-3,5), respectively, is discussed (for details in the preparation of **4** see Ref. [5]). Following the Sonogashira cross-coupling protocol [2d], **3** is accessible by heating $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{I})_2$ (**1**) with two equivalents of $\text{HC}\equiv\text{C-1-C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-3,5}$ (**2**) in presence of catalytic amounts of $[(\text{Ph}_3\text{P})_2\text{PdCl}_2/\text{CuI}]$ and diisopropylamine as solvent (Eq. (1)). After appropriate work-up, complex **3** could be isolated in 9% yield as a red-brown oil.



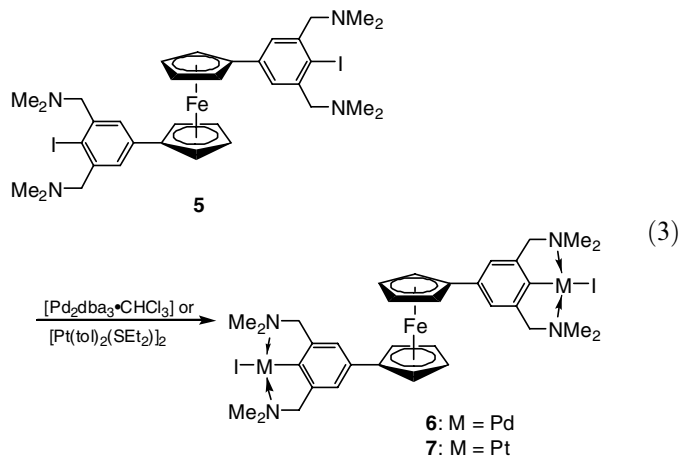
The standard procedure involving lithiation-*transmetalation* for the synthesis of palladium- and platinum-NCN pincers [8], however, could not be applied for the preparation of $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-C}\equiv\text{C-4-NCN-1-MX})_2$ (M = Pd, Pt; X = Cl, Br), since lithiation of **3** by either ^tBuLi or ⁱBuLi appears not possible. A similar behavior has been observed for the metallation of the bifero-cene $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4)(\eta^5\text{-C}_5\text{H}_4\text{-C}\equiv\text{C-NCNH})_2]$ [3,9]. This shows that other, competitive reactions occur.

In contrast, lithiation of $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-NCNH})_2$ (**4**) is possible by addition of two equivalents of ⁿBuLi to this compound. Dilithiated $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-4-NCN-1-Li})_2$ (**4**·Li) reacts with diiodine to form the orange colored sandwich complex $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-4-NCN-1-I})_2$ (**5**) which was isolated in 86% yield (Eq. (2)).



Oxidative addition of the C–I bond in **5** to palladium(0) is possible by reacting **5** with $[\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3]$ (dba = dibenzylidene acetone) in a 1:1 molar ratio in benzene for

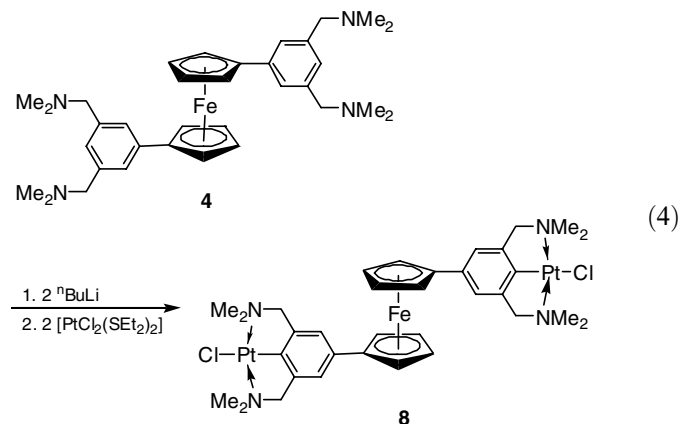
18 h at 25 °C. After appropriate work-up, orange colored $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-4-NCN-1-PdI})_2$ (**6**) was isolated in 68% yield (Eq. (3)). Isostructural $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-4-NCN-1-PtI})_2$ (**7**) is accessible by refluxing **5** with stoichiometric amounts of $[\text{Pt}(\text{tol})_2(\text{SEt}_2)_2]$ (tol = 4-tolyl) in toluene for 5 min (Eq. (3)). On addition of *n*-hexane to the reaction mixture, complex **7** precipitates as an orange solid.



Trimetallics **6** and **7** can also be obtained, when **4** is subsequently reacted with ⁿBuLi, I₂ and either $[\text{Pd}_2(\text{dba})_3]$ or $[\text{Pt}(\text{tol})_2(\text{SEt}_2)_2]$ (**6**: 58%, **7**: 48%).

Attempts to prepare FePd and FePt complexes or even heterotrimetallic FePdPt species by the stepwise insertion of the appropriate transition metals into the C_{aryl}–I bond(s) in **5**, however, did always result in the formation of 1:1 mixtures of **5** and **6**, and **5** and **7**, respectively. This clearly shows that the presence of a palladium or platinum atom in $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-NCN-I})(\eta^5\text{-C}_5\text{H}_4\text{-NCN-MI})$ (M = Pd, Pt) significantly activates the C–I bond towards the second oxidative addition.

As reported previously, trimetallic $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-4-NCN-1-PdCl})_2$ can be prepared from **4** by a lithiation-*transmetalation* sequence [1]. In a similar manner, orange-brown colored $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-4-NCN-1-PtCl})_2$ (**8**) appeared accessible by the subsequent reaction of **4** with ⁿBuLi and $[\text{PtCl}_2(\text{SEt}_2)_2]$ and was isolated in an overall yield of 15% (Eq. (4)).



Complexes **3** and **5–8** were characterized by elemental analysis, ¹H and ¹³C{¹H} NMR spectroscopy.

The ^1H NMR spectra of **3** and **5** reveal the resonance pattern typical for *non*-metallated pincer complexes [5,8b,10]. The CH_2 and NMe_2 protons appear as singlets at 3.45 and 2.28 ppm for **3** and at 3.26 and 2.12 ppm for **5**. The coordination of the Me_2NCH_2 nitrogen atoms to either a Pd(II) (**6**) or Pt(II) ion (**7**, **8**) results in a significant low-field shift of the CH_2 (**6**: 4.03, **7**: 4.08, and **8**: 4.05 ppm) and NMe_2 signals (**6**: 3.08, **7**: 3.25, and **8**: 3.13 ppm). Due to the increased electron density at the benzene ring a high-field shift of the aromatic protons from 7.01 (**5**) to ca. 6.8 ppm (**6–8**) is observed. For **7** and **8** typical ^{195}Pt satellites were found with coupling constants of ca. 36 ($^3J_{\text{PtH}(\text{Me})}$) and 42 Hz ($^3J_{\text{PtH}(\text{CH}_2)}$), respectively.

Upon complexation of the Me_2NCH_2 unit to M a characteristic downfield shift is observed in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (i.e. **5**: 68.9 (NCH_2), 45.4 ppm (NCH_3) vs. **6**: 74.1 and 55.0 ppm, respectively) (Experimental part).

2.2. Electrochemical studies

Cyclic voltammetric studies were carried out for **8** in acetonitrile and for **6** and **7** in tetrahydrofuran solutions at 25 °C. For comparison, also **4** and **5** were subjected to cyclic voltammetric measurements. Exemplary, the cyclic voltammograms of **5** and **6** are depicted in Fig. 1.

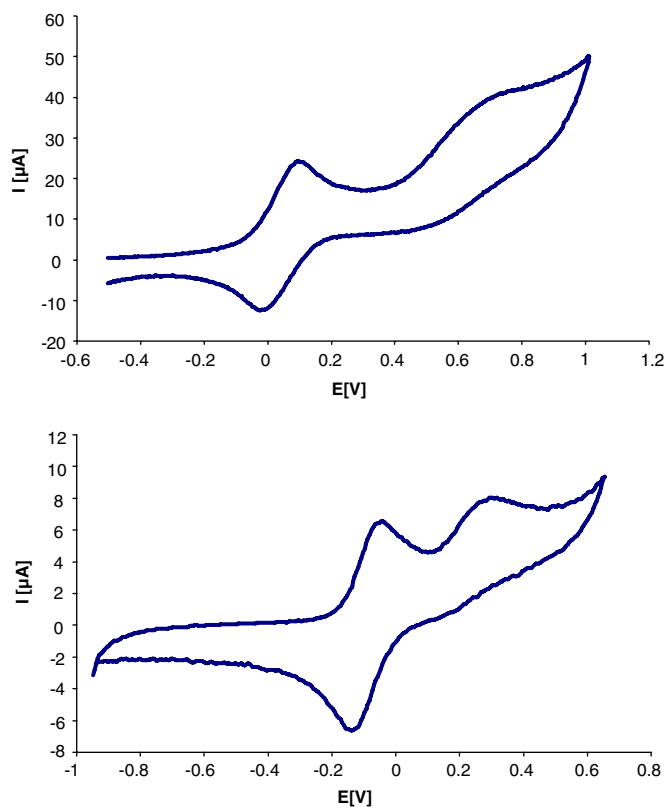


Fig. 1. Cyclic voltammograms of **5** (top) and **6** (bottom) in tetrahydrofuran in the presence of $[\eta\text{-Bu}_4\text{N}][\text{PF}_6]$ ($c = 0.10$ M), 25 °C, argon, scan rate = 200 mV s^{-1} . All potentials are referenced to the $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$ redox couple as standard ($\text{Cp}_2\text{Fe} = (\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$, $E_{1/2} = 0.00$ V).

Table 1
Electrochemical data of **4–8**

Compound	$E_{1/2}$ (V)	ΔE (mV)	E_{ox} (V)
$\text{Fe}(\text{C}_5\text{H}_4\text{-NCN-H})_2$ (4) ^a	+0.03	80	+0.76
$\text{Fe}(\text{C}_5\text{H}_4\text{-NCNH})_2$ (4) ^b	+0.01	80	+0.73
$\text{Fe}(\text{C}_5\text{H}_4\text{-NCN-I})_2$ (5) ^b	+0.04	131	+0.75
$\text{Fe}(\text{C}_5\text{H}_4\text{-NCN-PdI})_2$ (6) ^b	-0.09	96	+0.30
$\text{Fe}(\text{C}_5\text{H}_4\text{-NCN-PtI})_2$ (7) ^b	-0.16	106	n. obs. ^c
$\text{Fe}(\text{C}_5\text{H}_4\text{-NCN-PtCl})_2$ (8) ^a	-0.06	180	+0.70

^a In acetonitrile.

^b In tetrahydrofuran.

^c n. obs. = not observed.

Complexes **4–8** show reversible waves for the Fe(II)/Fe(III) redox couples (Fig. 1, Table 1).

The Fe(II)/Fe(III) potentials in monometallic **4** and **5** are as compared to the $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$ redox couple ($\text{FeCp}_2 = \text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$), shifted to a more positive value, which can be explained by the presence of the somewhat stronger electron withdrawing NCN groups in **4** and **5** rather than in ferrocene which has been taken as standard [5,11].

Upon complexation of the NCN pincer unit to either palladium or platinum (**6–8**) the energy of the Fe(II)/Fe(III) couple is shifted to a more negative value (Table 1). In this respect, complex **6** shows a reversible wave at -0.09 V ($\Delta E = 96$ mV) which is shifted by -130 mV as compared to **5** (Table 1). This confirms that the Fe(II) ion in **6** is somewhat easier to oxidize which is most likely caused by the *ortho*-metallation of the NCN pincer moiety (neutral vs. anionic NCN). An even more negative potential is found for **7** ($E_{1/2} = -0.16$ V, $\Delta E = 106$ mV) (Table 1). Although, these studies were performed in tetrahydrofuran solutions, a similar behavior is found, when the measurements were carried out in acetonitrile (Table 1). The difference in the redox potentials for **4** and **8** is with -90 mV somewhat smaller as compared to measurements done in tetrahydrofuran (vide supra). The irreversible anodic wave results from the oxidation of the NCN pincer units [5]. An analogous behavior has been reported for benzyl amine [12].

2.3. Solid state structure of **6**

Single crystals of **6** suitable for X-ray structure analysis could be obtained by slow distillation of *n*-hexane into a dichloromethane–chloroform mixture (ratio 1:1) containing **6** at -30 °C. The molecular structure of **6** is shown in Fig. 2. Geometric details are listed in Table 2 and experimental crystal data in Table 3 (Experimental part).

Complex **6** crystallizes in the monoclinic space group $\text{P2}_1/\text{c}$. The asymmetric unit contains half of the molecule with the second part generated by $-x + 1$, $-y + 1$, and $-z + 1$. The main geometric features of **6** resemble the structural data characteristic for ferrocene and NCN pincer complexes [8,10]. The Fe1 atom is located at an inversion center in crystals of **6** and gives rise to a rotation of

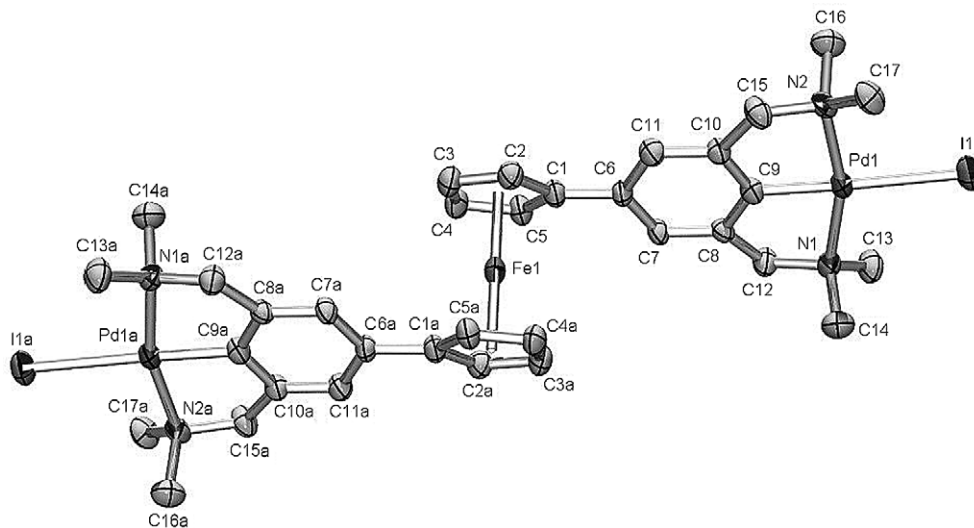


Fig. 2. POV-Ray plot (50% probability level) of **6** with the molecular geometry and atom numbering scheme. The hydrogen atoms, the chloroform and dichloromethane molecules have been omitted for clarity.

Table 2
Selected bond distances (Å), angles (°), and torsion angles (°) for **6**^a

Bond lengths		Bond angles		Torsion angles	
Pd1–I1	2.733(1)	I1–Pd1–C9	117.0(2)	C9–C8–C12–N1	21.1(7)
Pd1–C9	1.929(6)	N1–Pd1–N2	162.5(2)	C9–C10–C15–N2	22.8(8)
Pd1–N1	2.117(5)	N1–Pd1–I1	98.2(1)	Pd1–N1–C12–C8	–26.3(6)
Pd1–N2	2.126(5)	N2–Pd1–I1	99.3(1)	Pd1–N2–C15–C10	–28.1(6)
Fe1–D1 ^b	1.661(1)	C1–C13–N3	178.4(6)		

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

^b D1: centroid of the cyclopentadienyl ligands.

the two cyclopentadienyl ligands of the ferrocene moiety by 180° resulting in a staggered conformation. With the two NCN–PdI moieties pointing in opposite directions, no (π)-stacking of the C₆H₂ rings (C6–C11) was found either intra- or intermolecular as it has been observed for other 1,1'-bis-aryl- or 1,1'-bis-ethynylaryl-substituted ferrocenes [13]. A possible intermolecular interaction of the π -systems is further restricted, because of solvent molecules (dichloromethane and chloroform) incorporated in the crystal, separating single molecules of **6**.

The plane spanned by the C₆H₂ entity is tilted by 23.5(3)° towards the η^5 -coordinated C₅H₄ group. In the solid state structure this orientation averts an optimal overlap between the π -orbitals of the cyclopentadienyl and the NCN–PdI pincer fragments [14]. However, in solution the NCN pincer and cyclopentadienyl rings are free to rotate (vide supra).

Furthermore, the d⁸-configured Pd(II) ions are, as expected, coordinated in a slightly distorted square-planar fashion by the two nitrogen atoms N1 and N2, the NCN C_{ipso} carbon atom C9 and the iodine ligand I1. The coordination plane around Pd1 is almost coplanar with the plane of the C₆H₂ ring (10.3(3)°). The C9–Pd1–I1 bond angle is with 177.0(2)° linear, while N1–Pd1–N2 is with 162.5(2)° deformed from linearity.

3. Experimental section

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. Diisopropylamine 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 at 250.12 MHz and ¹³C{¹H} NMR at 62.86 MHz) and a Varian Inova 300 spectrometer (¹H NMR at 300.10 MHz and ¹³C{¹H} NMR at 75.47 MHz) in the Fourier transform mode. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane ($\delta = 0.00$ ppm) with the solvent as the reference signal (CDCl₃: ¹H NMR, $\delta = 7.26$; ¹³C{¹H} NMR, $\delta = 77.0$). Cyclic voltammograms were recorded in a dried cell purged with purified argon at 25 °C. Platinum wires served as working electrode and as counter electrode. A Ag/AgCl (or saturated calomel) electrode served as reference electrode. For ease of comparison, all potentials are converted using the redox potential of the ferrocene–ferr-

Table 3
Crystal and intensity collection data for **6**

Empirical formula	C _{37.5} H ₄₉ Cl ₉ FeI ₂ N ₄ Pd ₂
Chemical formula	C ₃₄ H ₄₄ FeI ₂ N ₄ Pd ₂
Formula weight	1397.31
Crystal system	Monoclinic
Space group	P2 ₁ /c
<i>a</i> (Å)	6.0803(3)
<i>b</i> (Å)	32.5876(15)
<i>c</i> (Å)	12.5281(6)
<i>V</i> (Å ³)	2431.9(2)
β (°)	101.574(1)
ρ_{calc} (g cm ⁻³)	1.908
F(000)	1358
Z	2
Crystal dimensions (mm)	0.2 × 0.1 × 0.1
Radiation (λ , Å)	Mo-K α (0.71073)
Absorption correction	Semi-empirical from equivalents
Maximum, minimum transmission	0.99999, 0.65934
Absorption coefficient (μ , mm ⁻¹)	2.822
Temperature (K)	193(2)
Scan range (°)	1.77 ≤ Θ ≤ 26.43
Index ranges	-7 ≤ <i>h</i> ≤ 7, 0 ≤ <i>k</i> ≤ 40, 0 ≤ <i>l</i> ≤ 15
Total reflections	20,931
Unique reflections	5102
Observed reflections [<i>I</i> ≥ 2 σ (<i>I</i>)]	4990
Refinement method	Full-matrix, least-squares (<i>F</i> ²)
Refined parameters	263
Restraints	16
Completeness to θ_{max}	99.7%
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> ≥ 2 σ (<i>I</i>)]	0.0479, 0.1173 ^a
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0590, 0.1222 ^b
<i>R</i> _{int} , <i>S</i>	0.0395, 1.046
Maximum, minimum peaks in final Fourier map (e Å ⁻³)	1.554, -1.199

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR_2 = \sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}} \text{ with } w = \frac{1}{\sigma^2(F_o^2) + (g_1 P)^2 + g_2 P}; P = \frac{(\max(F_o^2, 0) + 2F_c^2)}{3}$$

ocenium couple Cp₂Fe/Cp₂Fe⁺ (Cp₂Fe = (η^5 -C₅H₅)₂Fe) as the reference (*E*_{1/2} = 0.00 V) [15]. A conversion of the given data to the standard normal hydrogen electrode is possible following the suggestion made by Strehlow et al. [16]. Electrolyte solutions were prepared from freshly distilled acetonitrile or tetrahydrofuran solutions and [*n*-Bu₄N]PF₆ (dried in *oil-pump vacuum* at 120 °C, *c* = 0.1 M). The appropriate organometallic complexes were added at *c* = 1 mM. Cyclic voltammograms were recorded at a scan rate of 200 mV s⁻¹ using a Princeton Applied Research EG&G 263A analyzer or a Radiometer Copenhagen DEA 101 Digital Electrochemical analyzer with an IMT 102 Electrochemical Interface. Melting points were determined using sealed nitrogen purged capillaries on a Gallenkamp MFB 595 010 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, University of Technology.

3.2. General remarks

Fe(η^5 -C₅H₄I)₂ (**1**) [17], HC≡C-1-C₆H₃(CH₂NMe₂)₂-3,5 (**2**) [18], Fe(η^5 -C₅H₄-NCNH)₂ (**4**) [5], [PtCl₂(SEt₂)₂] [19], [Pd₂(dba)₃ · CHCl₃] [20], and [Pt(4-tol)₂(SEt₂)₂] [21] were prepared following published procedures. All other chemicals are commercially available and were used as received.

3.2.1. Synthesis of **3**

Compound **1** (920 mg, 2.10 mmol) and 960 mg (4.44 mmol) of **2** were dissolved in 30 mL of diisopropylamine and 124 mg (0.18 mmol, 4.0 mol%) of [PdCl₂(Ph₃P)₂] and 33 mg (0.18 mmol, 4 mol%) of [Cu(OAc)₂ · H₂O] were added. After heating the reaction mixture for 6 h to reflux all volatiles were removed (*oil-pump vacuum*). The reddish-brown solid was dissolved in 100 mL of diethyl ether and filtered through a pad of Silica gel (7 × 5 cm). With diethyl ether as eluent, 320 mg (0.73 mmol, 35% based on **1**) of **1** could be recovered. With tetrahydrofuran complex **3** was obtained as a red-brown oil. For further purification, **3** was dissolved in 100 mL of diethyl ether and this solution was extracted with 100 mL of water containing 5 mL of 4 M HCl. The aqueous phase was then separated, treated with 30 mL of 1 M NaOH and extracted twice with 100 mL of diethyl ether. The combined organic phases were dried over MgSO₄, filtered and all volatiles were evaporated in *oil-pump vacuum*. Yield: 120 mg (0.20 mmol, 9% based on **1**).

IR (NaCl): (cm⁻¹) 2221 (s) ($\nu_{\text{C}\equiv\text{C}}$). ¹H NMR (CDCl₃): [δ] 2.28 (s, 24H, NMe₂), 3.45 (s, 8H, CH₂N), 4.24 (pt, *J*_{HH} = 1.8 Hz, 4H, C₅H₄), 4.45 (pt, *J*_{HH} = 1.8 Hz, 4H, C₅H₄), 7.25 (s, 2H, C₆H₃), 7.39 (s, 4H, C₆H₃). ¹³C{¹H} NMR (CDCl₃): [δ] 45.3 (NCH₃), 63.9 (NCH₂), 67.5 (¹C/C₅H₄), 70.9 (CH/C₅H₄), 72.1 (CH/C₅H₄), 86.7 (FcC≡C), 86.9 (FcC≡C), 123.3 (¹C/C₆H₃), 129.1 (CH/C₆H₃), 130.5 (CH/C₆H₃), 138.9 (¹C/C₆H₃). Anal. Calc. for C₃₈H₄₆FeN₄ (614.63): C, 74.23; H, 7.55; N, 9.12. found: C, 73.95; H, 7.65; N, 8.98.

3.2.2. Synthesis of **5**

Complex **4** (170 mg, 0.21 mmol) was dissolved in 50 mL of *n*-hexane and 0.5 mL (0.8 mmol) of *n*BuLi (1.6 M in *n*-hexane) were added at 25 °C. After stirring for 16 h at this temperature all volatiles were removed in *oil-pump vacuum*. The orange residue was dissolved in 50 mL of diethyl ether and 300 mg (1.18 mmol) of I₂ were added at 0 °C. The reaction mixture was stirred upon warming to 25 °C for 8 h and quenched with 1.0 g of Na₂S₂O₃ dissolved in 50 mL of water. The organic phase was separated, extracted with 50 mL of water, dried over MgSO₄, filtered and evaporated in *oil-pump vacuum* to give **5** as an orange solid. Yield: 220 mg (0.27 mmol, 86% based on **4**).

M.p.: [°C] 139. ¹H NMR (CDCl₃): [δ] 2.12 (s, 24H, NMe₂), 3.26 (s, 8H, CH₂N), 3.82 (pt, *J*_{HH} = 1.8 Hz, 4H, C₅H₄), 4.35 (pt, *J*_{HH} = 1.8 Hz, 4H, C₅H₄), 7.01 (s, 4H, C₆H₂). ¹³C{¹H} NMR (CDCl₃): [δ] 45.4 (NCH₃), 67.8 (CH/C₅H₄), 68.9 (NCH₂), 70.7 (CH/C₅H₄), 84.8 (¹C/

C_5H_4), 104.0 (iC -I/ C_6H_2), 126.3 (CH / C_6H_2), 137.4 (iC / C_6H_2), 141.3 (iC / C_6H_2). Anal. Calc. for $C_{34}H_{44}FeI_2N_4$ (818.39): C, 49.90; H, 5.42; N, 6.85. found: C, 50.26; H, 5.71; N, 6.36.

3.2.3. Synthesis of 6

Compound **5** (100 mg, 0.122 mmol) and 125 mg (0.121 mmol) of $[Pd_2(dba)_3 \cdot CHCl_3]$ were dissolved in 15 mL of benzene and were stirred for 18 h at 25 °C. Afterwards, 20 mL of tetrahydrofuran were added and the reaction mixture was stirred for 4 h. All volatiles were removed (*oil-pump vacuum*) and the remaining greenish-black solid was dissolved in 30 mL of chloroform. The solution was filtered through a pad of Celite and concentrated to 3 mL (*oil-pump vacuum*). *n*-Hexane (30 mL) was then added, whereby an orange solid precipitated. The precipitate was collected and washed three times with *n*-hexane (10 mL) and diethyl ether (10 mL) to give **6** as an orange solid (85 mg, 0.082 mmol, 68% based on $[Pd_2dba_3 \cdot CHCl_3]$).

M.p.: [°C] 168 (dec). 1H NMR ($CDCl_3$): [δ] 3.08 (s, 24H, NMe_2), 4.03 (s, 8H, CH_2N), 4.12 (pt, $J_{HH} = 1.8$ Hz, 4H, C_5H_4), 4.41 (pt, $J_{HH} = 1.8$ Hz, 4H, C_5H_4), 6.78 (s, 4H, C_6H_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): [δ] 55.0 (NCH_3), 67.3 (CH/C_5H_4), 70.9 (CH/C_5H_4), 74.1 (NCH_2), 86.7 ($^iC/C_5H_4$), 117.7 (CH/C_6H_2), 135.2 ($^iC/C_6H_2$), 145.0 ($^iC/C_6H_2$), 149.5 ($^iC/C_6H_2$). Anal. Calc. for $C_{34}H_{44}FeI_2N_4Pd_2$ (1031.23): C, 39.60; H, 4.30; N, 5.43. Found: C, 39.68; H, 4.67; N, 5.50.

3.2.4. Synthesis of 7

Compound **5** (50 mg, 0.061 mmol) and 55 mg (0.059 mmol) of $[Pt(tol)_2(SEt_2)]_2$ were refluxed in 15 mL of toluene for 5 min. The orange solution was cooled to 25 °C, filtered through a pad of Celite 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 *n*-hexane (10 mL) and diethyl ether (10 mL) and dried in *oil-pump vacuum* to afford 40 mg (0.033 mmol, 56% based on $[Pt(tol)_2(SEt_2)]_2$) of **7** as an orange solid.

M.p.: [°C] 181. 1H NMR ($CDCl_3$): [δ] 3.25 (s, $^3J_{PtH} = 36.4$ Hz, 24H, NMe_2), 4.08 (s, $^3J_{PtH} = 41.7$ Hz, 8H, CH_2N), 4.14 (pt, $J_{HH} = 1.8$ Hz, 4H, C_5H_4), 4.43 (pt, $J_{HH} = 1.8$ Hz, 4H, C_5H_4), 6.76 (s, 4H, C_6H_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): [δ] 56.5 (NCH_3), 66.9 (CH/C_5H_4), 70.3 (CH/C_5H_4), 76.9 (NCH_2), 87.7 ($^iC/C_5H_4$), 117.3 (CH/C_6H_2), 133.4 ($^iC/C_6H_2$), 143.3 ($^iC/C_6H_2$), 147.7 ($^iC/C_6H_2$). Anal. Calc. for $C_{34}H_{44}Fe_2I_2N_4Pt_2 \cdot 2tol$ (1448.67): C, 39.80; H, 4.17; N, 3.87. Found: C, 40.40; H, 3.91; N, 3.39.

3.2.5. Synthesis of 8

Complex **4** (110 mg, 0.19 mmol) was dissolved in 30 mL of *n*-hexane and 0.24 mL (0.38 mmol) of tBuLi (1.6 M in *n*-hexane) were added at 25 °C. After this reaction mixture was stirred for 18 h at this temperature all volatiles were removed (*oil-pump vacuum*). The orange residue was dis-

solved in 30 mL of diethyl ether and 170 mg (0.38 mmol) of $[PtCl_2(Et_2S)_2]$ were added at 0 °C. The reaction mixture was stirred upon warming to 25 °C over night. All volatiles were removed in *oil-pump vacuum*. The dark brown residue was dissolved in 20 mL of dichloromethane and filtered through a pad of Celite. All volatiles were removed in *oil-pump vacuum* to give **8** as an orange–brown solid (30 mg, 0.03 mmol, 15% based on $[PtCl_2(Et_2S)_2]$).

M.p.: [°C] 175. 1H NMR ($CDCl_3$): [δ] 3.13 (s, $^3J_{PtH} = 34.4$ Hz, 24H, NMe_2), 4.05 (s, $^3J_{PtH} = 41.0$ Hz, 8H, CH_2N), 4.12 (pt, $J_{HH} = 1.8$ Hz, 4H, C_5H_4), 4.41 (pt, $J_{HH} = 1.8$ Hz, 4H, C_5H_4), 6.80 (s, 4H, C_6H_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): [δ] 55.0 (NCH_3), 67.3 (CH/C_5H_4), 70.9 (CH/C_5H_4), 74.1 (NCH_2), 86.7 ($^iC/C_5H_4$), 117.7 (CH/C_6H_2), 135.2 ($^iC/C_6H_2$), 145.0 ($^iC/C_6H_2$), 149.5 ($^iC/C_6H_2$). Anal. Calc. for $C_{34}H_{44}Cl_2FeN_4Pt_2$ (1025.65): C, 39.81; H, 4.32; N, 5.46. Found: C, 40.25; H, 4.51; N, 5.18.

4. X-ray structure determination of 6

X-ray structure analysis measurements were performed with a BRUKER SMART CCD 1 k diffractometer at 193 K using oil-coated shock-cooled crystals [22]. Reflections were collected in the ω -scan mode in 0.4° steps and an exposition time of 40 s per frame. The structure was solved by direct methods using SHELXS-97 [23] and refined by full-matrix least-square procedures on F^2 using SHELXL-97 [24]. All *non*-hydrogen atoms were refined anisotropically. All hydrogen atom positions were refined using a riding model. The dichloromethane molecule nearby the inversion centre is not fully present and has been refined to an occupancy of 0.77, while fixed to 0.75 at the end of the refinement. The structure plot was performed with POV-Ray [25]. The figures in parenthesis after each calculated value represent the standard deviation in units of the last significant digit(s).

5. Supplementary material

The crystallographic data for **6** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-612578. Copies of this information can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1ET, UK. [Fax: +44 1223 336033, e-mail: deposit@ccdc.cam.ac.uk].

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