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4-Ethinyl-benzonitrile-ferrocenes bridged by a $Pd(PPh_3)_2$ unit; the solid-state structure of $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4C{\equiv}CC_6H_4C{\equiv}N\text{-}1,4)$

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Abstract

The trinuclear Fc–Pd–Fc complex $[(FcC{\equiv}CC_6H_4C{\equiv}N\text{-}1,4)_2Pd(PPh_3)_2](OTf)_2$ (**5**) $[Fc = (\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)]$ is accessible by the reaction of $FcC{\equiv}CC_6H_4C{\equiv}N\text{-}1,4$ (**3**) with $(Ph_3P)_2Pd(OTf)_2$ (**4**) in a 2:1 molar ratio. In **5** the corresponding late transition metal centers are linked by $C_5H_4C{\equiv}CC_6H_4C{\equiv}N\text{-}1,4$ π-conjugated organic units. The result of the X-ray structure analysis of **3**, which itself can be synthesised by a Sonogashira coupling of $FcC{\equiv}CH$ (**1**) with $BrC_6H_4C{\equiv}N\text{-}1,4$ (**2**), is reported. Complex **3** crystallises in the monoclinic space group $P2_1$ with the following cell parameters: $a = 9.6598(6)$, $b = 7.3185(5)$, $c = 10.1910(7)$ Å, $\beta = 98.876(3)°$, $V = 711.80(8)$ Å^3 and $Z = 2$. In **3** the cyclopentadienyl ligands are rotated by 4.1(2)° and therefore possess an almost eclipsed conformation. With respect to the η^5-coordinated C_5H_4 group, the C_6H_4 unit is tilted by 69.87(13)°. Electrochemical studies on **3** show that the Fe(II)/Fe(III) oxidation process appears to be reversible and is shifted to a more positive value when compared to the FcH/FcH^+ couple. An even more positive value is observed for **5**. A reason for this behaviour is presented.

Keywords: Ferrocene; π-Conjugation; Metal–metal interaction; Cyclic voltammetry; X-ray structure analysis

1. Introduction

Recently, homo- and heterometallic transition metal complexes in which the appropriate metal centres are span by linear π-conjugated organic groups have attracted much attention, since they possess as new materials novel and/or interesting electronic properties. [1,2] For the synthesis of those complexes several synthetic strategies exist. One possible approach is given by the use of acetylenes which feature further potentially ligating sites, e.g. the benzonitrile group. The latter entity, allows the co-ordination of additionally transition metal complex fragments, giving rise to the formation of homo- and heterometallic species [3].

In this respect, we here describe the reaction of $FcC{\equiv}CC_6H_4C{\equiv}N\text{-}1,4$ $[Fc = (\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)]$ with $(Ph_3P)_2Pd(OTf)_2$ in an attempt to synthesise oligometallic transition metal complexes.

2. Results and discussion

2.1. Synthesis and spectroscopic characterisation

The 4-ethinyl-benzonitrile functionalised ferrocene $FcC{\equiv}CC_6H_4C{\equiv}N\text{-}1,4$ (**3**) $[Fc = (\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)]$ was first synthesised by Perry and coworkers, but to the best of our knowledge neither experimental details nor spectroscopic properties of **3** were reported [4]. One means to prepare **3** is given by the reaction of $FcC{\equiv}CH$ (**1**) with $BrC_6H_4C{\equiv}N\text{-}1,4$ (**2**) in a 1:1 molar ratio in the presence of catalytic amounts of $(Ph_3P)_2PdCl_2$–CuI in $HN(^iC_3H_7)_2$ as solvent (Scheme 1). In this Sonogashira coupling [5], mononuclear **3** is produced in 84% yield.

Orange coloured **3** is also accessible under similar reaction conditions in NEt_3 solutions, instead of $HN(^iC_3H_7)_2$, however, the yield is thereby lowered by ca. 10%.

Mononuclear **3** serves as the basis for the preparation of bi- or oligonuclear ferrocene-based transition metal complexes, e.g. the synthesis of $[(FcC{\equiv}CC_6H_4C{\equiv}N\text{-}1,4)_2Pd(PPh_3)_2](OTf)_2$ (**5**). The synthesis of the latter

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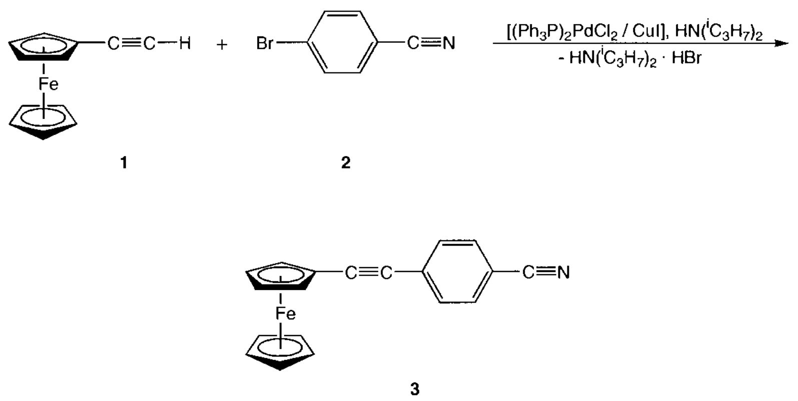


Scheme 1.

trimetallic complex was conducted following well-documented procedures, e.g. the preparation of molecular squares based on Group 10 transition metal atoms [6].

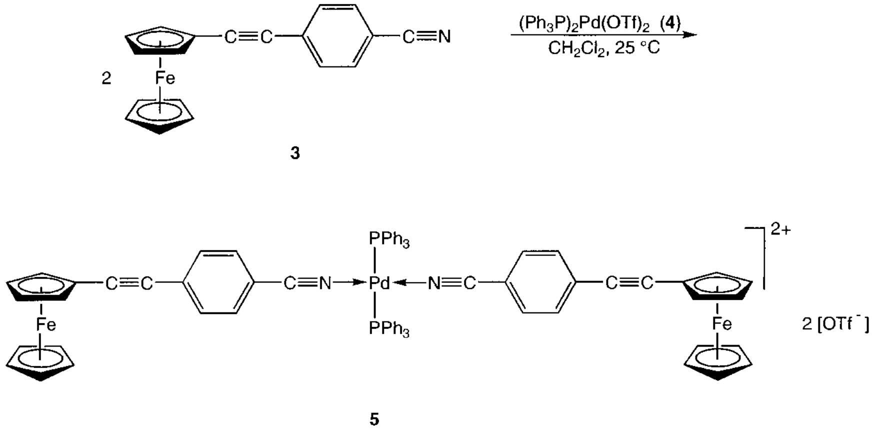
Thus, complex **3**, which features the $C\equiv N$ unit as N-ligating site, was reacted with neutral $(Ph_3P)_2Pd(OTf)_2$ (**4**) in a 2:1 molar ratio in dichloromethane as solvent. Upon replacement of the only weakly bonded OTf^- ligands in **4** by the $C\equiv N$ group of **3** the dicationic trinuclear Fc–Pd–Fc complex $[(FcC\equiv CC_6H_4C\equiv N\text{-}1,4)_2Pd(PPh_3)_2](OTf)_2$ (**5**) is formed in 66% yield (Scheme 2).

In **5** the Pd(II) center with a d^8 electron configuration possesses a square-planar environment, caused by the PPh_3 moieties and the organometallic building blocks $FcC\equiv CC_6H_4C\equiv N\text{-}1,4$, which are *trans*-configurated to each other. Thereby, the $C_5H_4C\equiv CC_6H_4C\equiv N\rightarrow Pd\leftarrow N\equiv CC_6H_4C\equiv CC_5H_4$ array is orientated in a linear manner.

The $C\equiv N$ stretching vibration in the IR spectra of **3** and **5** is a most informative spectroscopic tool for monitoring the progress of the reaction of **3** with **4** to yield **5**. In this respect, the $\nu_{C\equiv N}$ absorption band typical for **5** has been shifted to higher wavenumbers (2276 cm^{-1}) as compared to that of the starting material **3** (2223 cm^{-1}), indicating a dative bonding of the $C\equiv N$ groups to the Pd(II) centre in **5**. This observation resembles the data found for other transition metal complexes such as $\{[(dppp)Pd][C_6H_4(C\equiv N)_2\text{-}1,4]_2\text{-}[OTf]_2\}_4$ (2280 cm^{-1}) [dppp = 1,3-bis(diphenylphosphino)propane)] [6].

In contrast thereto, the stretching vibrations for the $C\equiv C$ moieties found at ca. 2200 cm^{-1} for **3** and **5** are not affected.

The comparison of the ^1H-NMR spectra of **3** and **5** reveals that the resonance signals of the cyclopentadienyl protons appear virtually at almost the same values with a singlet for the C_5H_5 group at 4.25 ppm and two pseudo-triplets for the C_5H_4 unit at 4.30 as well as 4.53 ppm with a coupling constant of $J_{HH} = 1.9$ Hz. The resonance signals of the C_6H_4 and C_6H_5 groups are found in the expected region between 7.3 and 7.7 ppm as multiplets.



Scheme 2.

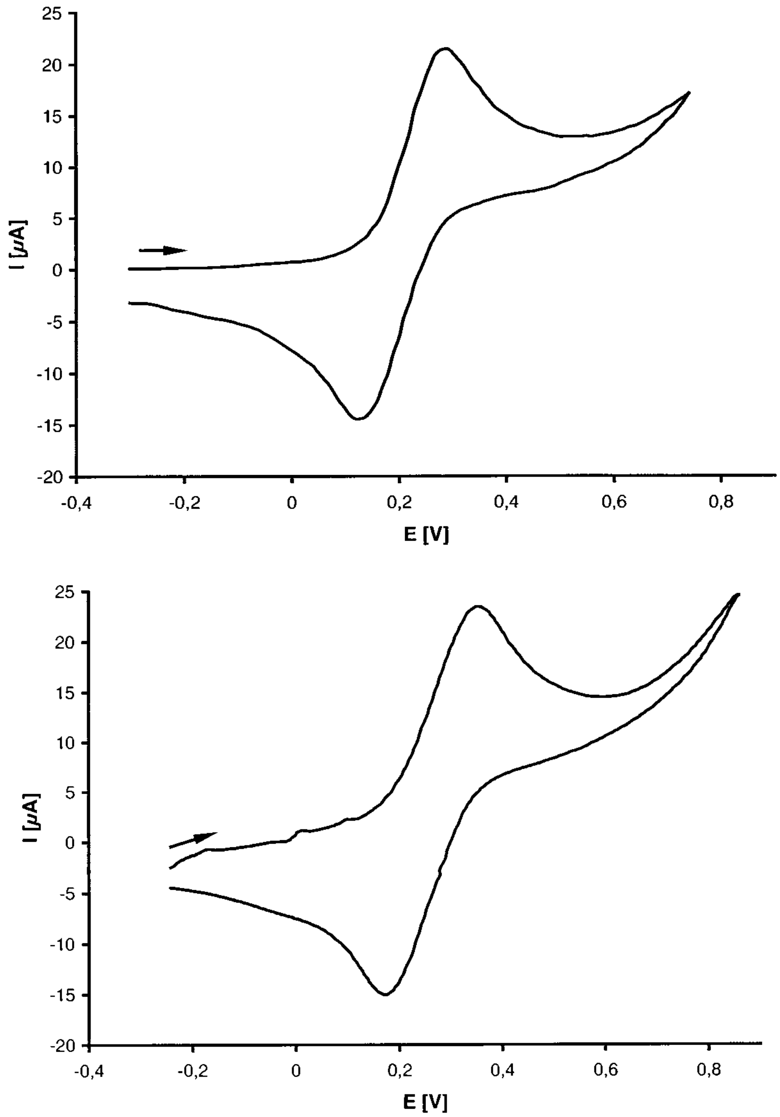


Fig. 1. Cyclic voltammogramms of **3** (top) and **5** (bottom) in tetrahydrofuran solutions at 25 °C.

In the $^{13}C\{^1H\}$-NMR spectrum of **3** sharp and well-resolved resonance signals for the organic groups are found in the expected region. Nevertheless, due to the high instability of **5** in solution (vide supra), only the signals of the cyclopentadienyl groups could clearly be assigned.

In $^{31}P\{^1H\}$-NMR studies carried out on complexes **4** and **5** it was also observed, as the IR studies do, that the C≡N substituents are datively bonded to the Pd(II) centre in **5**. This has been inferred by a shift of the ^{31}P resonance signal from 40.0 ppm in **4** to 36.4 ppm in **5** [6].

2.2. Electrochemical studies

Cyclovoltammetric studies were carried out on mononuclear **3** and trinuclear **5** in THF solutions at 25 °C. The obtained cyclic voltammograms are depicted in Fig. 1.

It was found that the Fe(II)/Fe(III) oxidation ($E_{Ox} = +0.18$ V, $\Delta E = 150$ mV) in **3** is reversible (Fig. 1), and is, as compared to the FcH/FcH$^+$ redox-couple, shifted to a more positive value. This displacement can be interpreted by means of a stronger electron-withdrawing group present in **3** than in FcH, taken as standard [7].

The cyclic voltammogram of **5** also exhibits a reversible Fe(II)/Fe(III) couple at $E_{Ox} = +0.26$ V ($\Delta E = 200$ mV). This couple is shifted by ca. 0.08 V to a more positive value when compared with **3**. This shifting confirms that the iron centre in **5** is more difficult to oxidise which is attributed to the electron-withdrawing properties of the $Pd(PPh_3)_2$ bridging unit [8].

2.3. Solid-state structure of 3

Single crystals of **3** suitable for X-ray structure analysis were obtained by slow evaporation of a Et_2O solution at −30 °C. Mononuclear **3** crystallises in the monoclinic space group $P2_1$ with $a = 9.6598(6)$, $b = 7.3185(2)$, $c = 10.1910(7)$ Å, $\beta = 98.876(2)°$, $V = 711.80(8)$ Å^3 and $Z = 2$. The molecular structure of **3** is shown in Fig. 2. Geometric details are listed in Table 1 and experimental crystal data in Table 2.

The main structural features of **3** combine the structural results, characteristic for alkinyl-ferrocenyl derivatives [1,2b,9] with a one-dimensional linear $C_5H_4C{\equiv}CC_6H_4C{\equiv}N$ arrangement (Fig. 2). The Fe(1)–D(1) as well as the Fe(1)–D(2) separations [D(1), D(2) = centroids of the cyclopentadienyl ligands C_5H_4 and C_5H_5, respectively] with 1.640(2) and 1.644(2) Å are in agreement with the values found for other well-known ferrocene complexes. [1,2b,7,9] The two cyclopentadienyl ligands are thereby rotated by 4.1(2)° to each other, which verifies an almost eclipsed conformation. A further noticable feature of the π-conjugated organic $C_5H_4C{\equiv}CC_6H_4C{\equiv}N$ unit is that the C_6H_4 entity is with 69.87(13)° tilted towards the η^5-coordinated C_5H_4 group. This orientation averts an optimal overlap between the π-orbitals of the cyclopentadienyl, ethinyl, phenyl and nitrile fragments [10]. However, this structural behaviour found in the solid-state is not in accordance with the one observed in oligometallic complexes, e.g. in which **3** is datively bonded to transition metal moieties. One example is $[(FcC{\equiv}CC_6H_4C{\equiv}N\text{-}1,4)Pt\text{-}\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}](OTf)$ of which the result of the X-ray structure analysis confirms that the appropriate C_5H_4 and C_6H_4 units are bonded in plane [11].

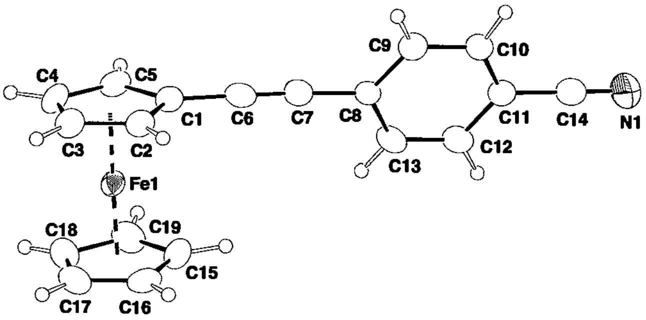


Fig. 2. ORTEP drawing (50% probability level) of **3** with the molecular geometry and atom numbering scheme.

Table 1
Selected bond lengths (Å) and bond angles (°) for **3** [a]

Bond lengths			
Fe(1)–D(1) [b]	1.640(2)	Fe(1)–D(2) [b]	1.644(2)
C(1)–C(6)	1.444(5)	C(6)–C(7)	1.190(5)
C(7)–C(8)	1.432(5)	C(11)–C(14)	1.448(5)
C(14)–N(1)	1.142(5)		
Bond angles			
D(1)–Fe(1)–D(2)	178.67	C(1)–C(6)–C(7)	177.9(4)
C(6)–C(7)–C(8)	177.2(4)	C(11)–C(14)–N(1)	179.5(4)

[a] Standard deviations are given as the last significant figure in parenthesis.

[b] D(1), D(2): centroids of the cyclopentadienyl ligands.

Table 2
Crystal data and structure refinement parameters for **3**

Empirical formula	$C_{19}H_{13}FeN$
Chemical formula	$C_{19}H_{13}FeN$
Formula weight	311.15
Temperature (K)	173(2)
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	
a (Å)	9.6598(6)
b (Å)	7.3182(5)
c (Å)	10.1910(7)
β (°)	98.876(2)
V (Å^3)	711.80(8)
Z	2
ρ_{calc} (g cm^{-3})	1.452
Absorption coefficient (μ, mm^{-1})	1.050
F(000)	320
Crystal dimensions (mm^1)	$0.36 \times 0.2 \times 0.08$
Theta range for data collection (°)	$2.02 \leq \theta \leq 30.81$
Scan mode	ω-scan
Index ranges	$-13 \leq h \leq 12$, $-10 \leq k \leq 10$, $-14 \leq l \leq 13$
Radiation (λ, Å)	Mo–K_α (0.71073)
Absorption correction	Empirical using SADABS
Max/min transmission	0.847243, 0.645055
Reflections collected	5283
Reflections observed [$I \geq 2\sigma(I)$]	2869
Unique reflections	3780
Refinement method	Full-matrix, least-squares (F^2)
Refined parameters	242
Completeness to θ_{max} (%)	89.6
Final R indices	$R_1 = 0.0444$, [a] $wR_2 = 0.0767$ $R_1 = 0.0700$, [a] $wR_2 = 0.0849$
R_{int}, S [a]	0.0293, 0.978
Max/min peaks in final Fourier map (e Å^{-3})	0.349/−0.455

[a] $R_1 = [\Sigma ((\|F_o| - |F_c|)/\Sigma|F_o|)]$; $wR_2 = [\Sigma (w(F_o^2 - F_c^2)^2)/\Sigma (wF_o^4)]^{1/2}$; $P = [F_o^2 + 2F_c^2]/3c)$; $S = [\Sigma w(F_o^2 - F_c^2)^2]/(n-p)^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0267P)^2 + 0.0000P]$; n = number of reflections, p = parameters used.

3. Experimental

3.1. General methods

All reactions were carried out under an atmosphere of purified nitrogen (O_2 traces: Cu catalyst, BASF AG, Ludwigshafen; H_2O: molecular sieve 4 Å) using standard Schlenk techniques. THF, Et_2O and n-pentane were purified by distillation from Na–benzophenone ketyl; CH_2Cl_2 was purified by distillation from P_2O_5 and diisopropylamine by distillation from KOH. IR spectra were recorded on a Perkin–Elmer FTIR 1000 spectrometer. ^{1}H-NMR spectra were recorded on a Bruker Avance 250 spectrometer operating at 250.123 MHz in the Fourier transform mode; $^{13}C\{^1H\}$-NMR spectra were recorded at 62.860 MHz. Chemical shifts are reported in δ units (ppm) downfield from tetramethylsilane with the solvent as the reference signal ($CDCl_3$: ^{1}H-NMR, $\delta = 7.26$; $^{13}C\{^1H\}$-NMR, $\delta = 77.0$). $^{31}P\{^1H\}$-NMR were recorded at 101.202 MHz in $CDCl_3$ with $P(OMe)_3$ ($\delta = 139.0$ ppm) as external reference relative to H_3PO_4 ($\delta = 0.0$ ppm). Melting points were determined using sealed nitrogen purged capillaries on a Büchi MP 510 melting point apparatus. Microanalyses were performed by the Department of Organic Chemistry at the Technical University of Chemnitz. Electrochemical measurements were carried out by cyclic voltammetry in $[n\text{-}Bu_4N][PF_6]$ solutions ($c = 0.1$ M) at 25 °C, using a standard three-electrode cell on a Radiometer Copenhagen DEA 101 Digital Electrochemical Analyser with a IMT 102 Electrochemical Interface. All potentials were referenced to the ferrocene/ferrocenium couple, which was used as internal reference with $E_{Ox} = 0.00$ V. ESI-TOF mass spectra were recorded on a Mariner ESI-TOF mass spectrometer (Applied Biosystems) operating in the positive-ion mode in a THF–MeOH solution.

3.2. General remarks

The starting materials FcC≡CH (**1**) [12], $(Ph_3P)_2Pd(OTf)_2$ (**4**) [13] were prepared following published procedures. All other chemicals were purchased from commercial sources.

3.3. Synthesis of *FcC≡CC$_6$H$_4$C≡N-1,4* (**3**) [4]

To 720 mg (3.43 mmol) of FcC≡CH (**1**), 50 mg (0.07 mmol) of $(Ph_3P)_2PdCl_2$ and 10 mg (0.05 mmol) of CuI in 20 ml of $HN(^iC_3H_7)_2$ were added 620 mg (3.4 mmol) of $BrC_6H_4C{\equiv}N$-1,4 (**2**) in one portion at 25 °C. After stirring the reaction mixture for 16 h at this temperature, all volatiles were removed in oil-pump vacuo. The resulting brown residue was then dissolved in 50 ml of Et_2O and filtered through a pad of Al_2O_3. The obtained orange solution was concentrated to 5 ml and crystallisation at −30 °C yielded **3** (890 mg, 84% based on **2**) as orange needles.

Melting point: 174 °C. IR (KBr, cm^{-1}) $\nu_{C\equiv N}$ 2223 (s), $\nu_{C\equiv C}$ 2202 (m). ^{1}H-NMR ($CDCl_3$) δ 4.25 (s, 5H, C_5H_5), 4.30 (pt, 2H, $J_{HH} = 1.9$ Hz, C_5H_4), 4.53 (pt, 2H, $J_{HH} = 1.9$ Hz, C_5H_4), 7.5–7.7 (m, 4H, C_6H_4). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 63.8 ($^iC/C_5H_4$), 69.4 (CH/C_5H_4), 70.1 (CH/C_5H_5), 71.7 (CH/C_5H_4), 84.5 (Fc*C*≡C), 93.9 (FcC≡*C*), 110.6 (*C*≡N), 118.7 ($^iC/C_6H_4$), 129.0 ($^iC/C_6H_4$), 131.7 (CH/C_6H_4), 132.0 (CH/C_6H_4). Anal. Found: C, 73.28; H, 4.39;N, 4.42. Calc. for $C_{19}H_{13}FeN$ (311.15): C, 73.34; H, 4.21; N, 4.50%.

3.4. X-ray structure determination of **3**

X-ray structure analysis measurements were performed on a BRUKER SMART CCD. Crystal data of **3** as well as data collection and refinement details are given in Table 2.

The unit cell was determined with the program SMART. [14] For data integration and refinement of the unit cell the program SAINT [14] was used. The space group was determined using the program ABSEN [15]. All data were corrected for absorption using SADABS [16]. The structure was solved using direct methods (SHELX-97 [17]), refined using Least-squares-methods (SHELX-97 [17]) and drawn using ZORTEP. [18]

All non-hydrogen atoms were fully refined in their located positions, the hydrogen atoms were taken from the electron density difference map and in their refined freely position as well as their thermal parameters. The figure in parenthesis after each calculated value represents the standard deviation in units of the last significant digit.

3.5. Synthesis of *[(FcC≡CC$_6$H$_4$C≡N-1,4)$_2$Pd(PPh$_3$)$_2$](OTf)$_2$* (**5**)

To 45 mg (0.05 mmol) of $(Ph_3P)_2Pd(OTf)_2$ (**4**) dissolved in 20 ml of CH_2Cl_2 were added 30 mg (0.1 mmol) of $FcC{\equiv}CC_6H_4C{\equiv}N$-1,4 (**3**) in one portion. On addition of **3** to **4** the colour of the reaction mixture changes immediately from colourless to brown. After stirring for 2 h at 25 °C, 10 ml of Et_2O were added and as a result thereof a brown precipitate was formed. This precipitate was filtered off and drying in vacuo afforded 50 mg (0.03 mmol, 66% based on **4**) **5** as a brown solid.

Melting point: 109 °C (dec.). IR (KBr, cm^{-1}): $\nu_{C\equiv N}$ 2276 (s), $\nu_{C\equiv C}$ 2203 (m), $\nu_{C\text{–}F}$ 1260 (s), $\nu_{SO,asym}$ 1172 (m), $\nu_{SO,sym}$ 1031 (s). ^{1}H-NMR ($CDCl_3$): δ 4.1–4.4 (bs, 10H, C_5H_5), 4.1–4.4 (bs, 4H, C_5H_4), 4.4–4.6 (bs, 4H, C_5H_4), 7.3–7.7 (m, 8H, C_6H_4), 7.3–7.7 (m, 30H, C_6H_5). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 69.8 (CH/C_5H_4), 69.9 (CH/C_5H_5), 73.0 (CH/C_5H_4).[1] $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 36.4. ESI-TOF MS; *m/z* (relative intensity): 1283.4 (5) $[M - 2OTf + OMe]^+$, 926.3 (15) $[M - 2OTf - PPh_3 - C_5H_5]^+$, 848.3 (100) $[M - 2OTf - PPh_3 - C_5H_5 - Ph]^+$, 807.3 (40) $[M - 2OTf - 2Fc - Ph]^+$. Anal. Found: C, 52.19; H, 4.17; N, 1.93. Calc. for $C_{76}H_{56}F_6Fe_2N_2O_6P_2PdS_2$ (1551.44): C, 58.84; H, 3.64; N, 1.81%.[1]

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[1] Due to the instability of **5** (vide supra) following its decomposition the signals for the other carbon atoms could not be unambiguously identified. In addition, the elemental analysis for the carbon value is not in accordance with the calculated one.

4. Supplementary material

Crystallographic data for the structural analysis (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 155756 for compound **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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