

Biferrocene NCN pincer metal-d⁸ complexes: Synthesis, reaction chemistry and cyclovoltammetric studies

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Abstract

The synthesis of biferrocene-bridged NCN pincer palladium and platinum complexes (NCN = [1-C₆H₂(CH₂NMe₂)₂-3,5][−]) is discussed. Sonogashira cross-coupling of [(η⁵-C₅H₄)Fe(η⁵-C₅H₄C≡CH)]₂ (**1**) with I-1-NCN-4-X (**2a**, X = H; **2b**, X = Br) produces [(η⁵-C₅H₄)Fe(η⁵-C₅H₄C≡C-1-NCN-4-X)]₂ (**3a**, X = H; **3b**, X = Br). Homobimetallic **3b** further reacts with [Pd₂(dba)₃ · CHCl₃] (**4**) or [Pt(tol)₂(SEt₂)₂] (**5**) (dba = dibenzylidene acetone, tol = 4-tolyl), respectively, to give tetrametallic [(η⁵-C₅H₄)Fe(η⁵-C₅H₄C≡C-4-NCN-1-MBr)]₂ (**6**, M = Pd; **7**, M = Pt) in which NCN-MBr fragments are connected by a biferrocene unit. Cyclovoltammetric studies show that the ferrocene moieties can independently be oxidized. The difference of the Fe(II)/Fe(III) redox couples amounts to ca. 300 mV and is not affected by the nature of the NCN pincer metal moieties.

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Keywords: Biferrocene; NCN pincer; Iron; Palladium; Platinum; Tetrametallic; Cyclovoltammetry

1. Introduction

Recently, one-dimensional homo- and heterometallic complexes in which the transition metal atoms are connected by π -conjugated organic and/or inorganic units have attracted great attention, due to their use as, for example, molecular wires [1], sensors [2], or organometallic polymers [3]. Complexes with reversibly switchable redox active sites are particularly of interest, because they can selectively adjust the electron density and electronic properties by oxidation or reduction. In this respect, biferrocene is a most promising candidate to be used as a switchable two-electron reservoir [4]. The redox-chemistry of biferrocene is characterized by two reversible one-electron couples and electronic communication between the two (η⁵-C₅H₅(η⁵-C₅H₄)Fe) moieties was found [4a]. Mono-oxidation of the latter species selectively leads to a mixed-valence Fe(II)–Fe(III) system with specific physical properties. X-

ray crystal structure analysis and, for example, ⁵⁷Fe Mössbauer spectroscopy of a mixed valent salt showed non-equivalence in the ferrocenyl building blocks [4d].

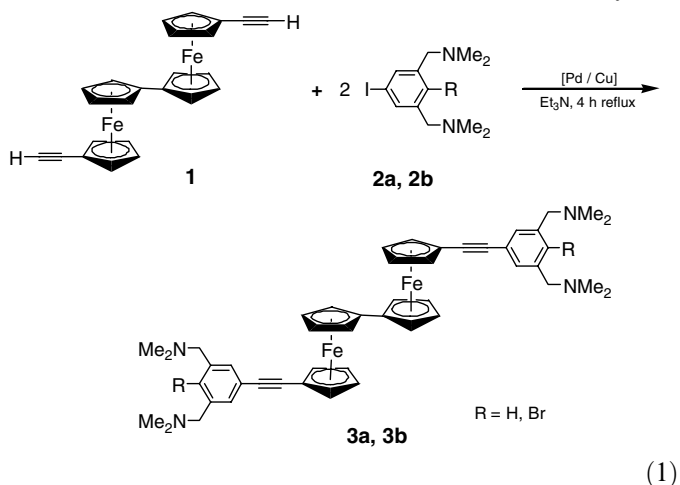
We here report on the synthesis and subsequent metallation of [(η⁵-C₅H₄)Fe(η⁵-C₅H₄C≡C-4-NCN-1-X)]₂ (NCN = [1-C₆H₂(CH₂NMe₂)₂-2,6][−]; X = H, Br) to give novel tetrametallic complexes of structural type [(η⁵-C₅H₄)Fe(η⁵-C₅H₄C≡C-4-NCN-1-MBr)]₂ (M = Pd, Pt). Our strategy was to use biferrocene as both bridging units and as redox center(s) between two NCN-MBr moieties, because only less is known about functionalized polyferrocene derivatives which is attributed to the difficulty in controlling the synthesis of such species.

2. Results and discussion

Following the Sonogashira cross-coupling protocol [5], [(η⁵-C₅H₄)Fe(η⁵-C₅H₄C≡CH)]₂ (**1**) produces with 1-I-C₆H₃(CH₂NMe₂)₂-3,5 (**2a**) and 1-I-C₆H₂(CH₂NMe₂)₂-3,5-Br-4 (**2b**) in the presence of catalytic amounts of

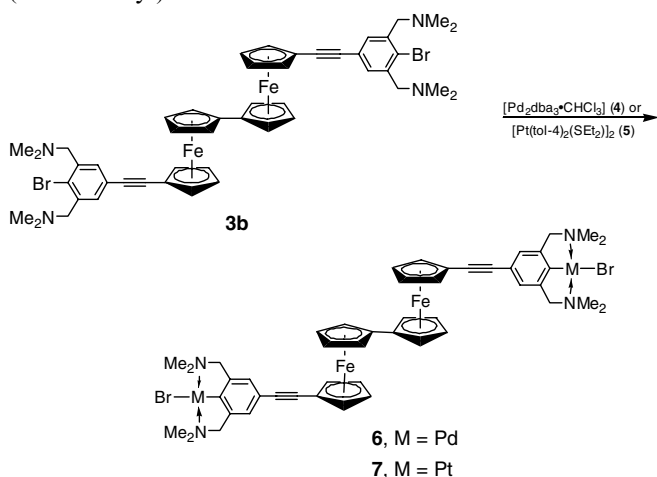
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$[(\text{Ph}_3\text{P})_2\text{PdCl}_2/\text{CuI}]$ in triethylamine as solvent the NCN-functionalized biferrocenes $[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{C}\equiv\text{C-4-NCN-1-X})_2]$ (NCN = $[1\text{-C}_6\text{H}_2(\text{CH}_2\text{NMe}_2)_2\text{-3,5}]^-$; **3a**, X = H; **3b**, X = Br) (Eq. (1)). After appropriate work-up, **3a** and **3b** can be isolated as red-brown solids in ca. 50% yield.



The standard lithiation–*trans*metallation procedure for the complexation of palladium or platinum by NCN pincers [6] could not be applied for **3a** and **3b**. Treatment of these species with $t\text{BuLi}$ to generate the corresponding dilithium derivatives followed by a quench with D_2O did not result in the formation of the respective deuterated NCN pincer molecules.

Another, and hence very effective option to prepare NCN pincer complexes with late transition metals involves the oxidative addition of carbon–bromide and –iodide bonds, respectively, to low-valent metal atoms M (M = Ni, Pd, Pt). [7] A suitable precursor for Pd(0) is $[\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3]$ (dba = dibenzylidene acetone) (**4**) [8]. Reacting **3b** with equimolar amounts of **4** for 18 h at 25 °C in benzene yielded tetrametallic $[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{C}\equiv\text{C-4-NCN-1-PdBr})_2]$ (**6**) in 66% yield (Eq. (2)). The preparation of the orange colored, iso-structural Fe_2Pt_2 complex $[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{C}\equiv\text{C-4-NCN-1-PtBr})_2]$ (**7**) could be realized by refluxing **3b** with stoichiometric amounts of the platinum source $[\text{Pt}(\text{tol-4})_2(\text{SEt}_2)_2]$ (**5**) (tol = 4-tolyl) in toluene.



The solubility of **3a**, **3b**, **6** and **7** strongly decreases with increasing molecular mass. Homobimetallic **3a** and **3b** are nicely soluble in benzene or diethyl ether, whereas tetrametallic **6** and **7** can only be dissolved in polar organic solvents such as dichloromethane, chloroform, tetrahydrofuran and acetonitrile, whereby **6** shows a somewhat better solubility than **7**. This can successfully be used in the purification of **6**, since this complex precipitates from dichloromethane or chloroform by adding *n*-hexane. Due to the lower solubility of **7** it was difficult to isolate analytical pure samples (Section 4). However, ESI-TOF mass spectrometric studies confirmed the proposed structure of **7** with M^+ at $m/e = 1346.2$. Further typical fragments are $\text{M}^+ - \text{C}_2\text{H}_4\text{PtBr}$ ($m/e = 1043.1$) and $\text{M}^+ - \text{C}_2\text{NCNPtBr} + \text{H}$ ($m/e = 851.1$).

Compounds **3a**, **3b** and **6** were characterized by IR, ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy and elemental analysis. The spectroscopic data for **7** are partly presented as well.

As expected, the ^1H NMR spectra of **3a**, **3b** and **6** in CDCl_3 show for the cyclopentadienyl protons two resonance signals with a AA'BB' pattern and coupling constants of 1.8 and 1.9 Hz, while for **7** only broad resonance signals could be detected. The CH_2 and NMe_2 protons of the NCN ligands appear as singlets (Section 4). Upon introduction of a palladium or platinum atom as given in complexes **6** and **7** a significant low-field shift of these resonances is observed (**3b**: 2.34, 3.53; **6**: 2.99, 3.99; **7**: 3.11, 4.01 ppm).

Most characteristic in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **3b** and **6** is the shift of the C(4) carbon atom to lower field, when going from **3b** ($\delta(\text{C-Br}) = 126.0$ ppm) to **6** ($\delta(\text{C-PdBr}) = 158.2$ ppm). This indicates that C(4) becomes deshielded, due to the presence of the palladium atom. Similar downfield shifts are also found for the CH_2 and NMe_2 carbons (Section 4).

In the IR spectra of **3a**, **3b**, **6** and **7** the $\text{C}\equiv\text{C}$ stretching vibrations is found at ca. 2210 cm^{-1} , showing that this absorption band is not affected by the introduction of palladium or platinum in **3**. An analogous behaviour has been observed for complexes with comparable structural elements such as $\{\text{Pt}\}(\text{C}\equiv\text{C})_n\{\text{Pt}\}$ ($n = 1, 2$; $\{\text{Pt}\} = 4\text{-C}_6\text{H}_2(\text{CH}_2\text{NMe}_2)_2\text{-2,6-PtCl-1}$) [6c].

Cyclovoltammetric studies were carried out with the homobimetallic NCN-functionalized biferrocenes **3a** and **3b** and the tetrametallic biferrocene NCN pincer metal- d^8 complexes **6** and **7** in tetrahydrofuran and dichloromethane solutions at 25 °C (Table 1). Exemplary, the obtained cyclic voltammograms for **3b** and **6** are depicted in Fig. 1.

The biferrocene-based transition metal compounds, **3a**, **3b**, **6** and **7** display the typical discrete one-electron, chemically reversible oxidation waves $E_{0,1}$ and $E_{0,2}$ of the ferrocenyl units in the cyclovoltammograms which can be assigned to the Fe(II)/Fe(III) redox couples (Table 1) [1e,4c,4d,9].

In **1** the two iron atoms can be reversibly oxidized at $E_{0,1} = +0.08\text{ V}$ and $E_{0,2} = +0.40\text{ V}$ [9a]. Compared to **3a** and **3b** these potentials are somewhat shifted to more

Table 1
Electrochemical data of **3a**, **3b**, **6** and **7**, and **1** for comparison

Compound	$E_{0,1}$ [V] (ΔE_p [mV])	$E_{0,2}$ [V] (ΔE_p [mV])	ΔE_0 [mV]	$K_c \text{Fe}_2$
Biferrocene [10]	−0.09	0.24	0.33	3.78×10^5
1 [9]	0.08 (70)	0.40 (75)	0.32	2.50×10^5
3a ^a	−0.05 (270)	0.24 (294)	0.29	0.80×10^5
3b ^a	0.02 (215)	0.32 (216)	0.30	1.37×10^5
3b ^b	−0.01 (112)	0.32 (156)	0.34	4.77×10^5
6 ^b	−0.03 (115)	0.28 (135)	0.31	1.54×10^5
7 ^b	−0.04 (202)	0.26 (188)	0.30	1.22×10^5

^a In tetrahydrofuran.

^b In dichloromethane.

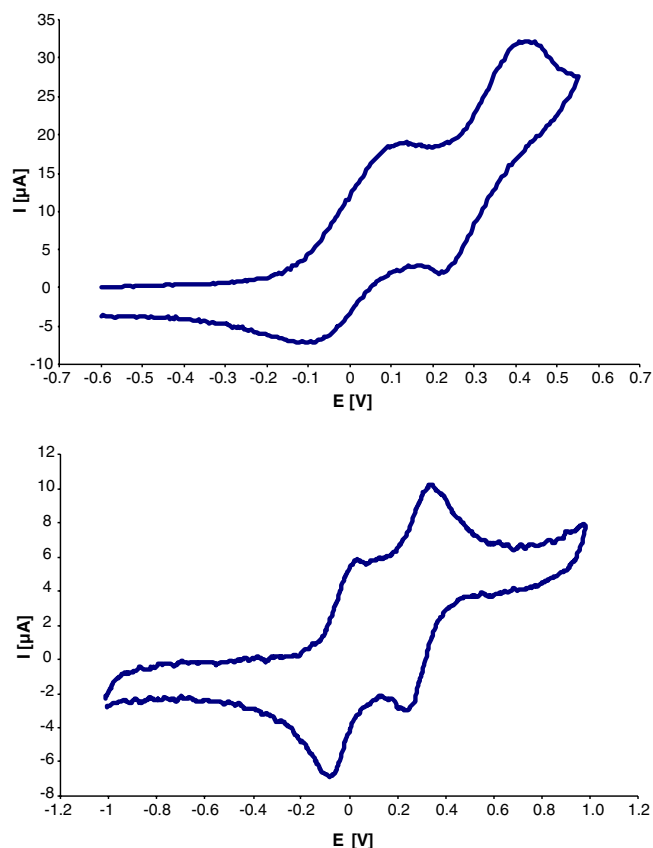


Fig. 1. Cyclic voltammograms of **3b** (top) and **6** (bottom) in dichloromethane in the presence of $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ ($c = 0.10$ M) at 25 °C under argon at a scan rate of 100 mV s^{-1} . Potentials are referenced to the $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$ couple as internal standard ($\text{Cp}_2\text{Fe} = (\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$, $E_0 = 0.00$ V).

negative values, indicating that the introduction of NCN pincer units at the biferrocene core only slightly influences the electron density at the iron centres. Compound **3a** is more difficult to oxidize (+70 mV for the 1st and +80 mV for the 2nd oxidation) than **3b**, which is attributed to the appropriate polarity of the C–H versus C–Br bond. The group-10 transition metals palladium and platinum in **6** and **7** also affect the redox potentials of the two biferrocene iron atoms. The increased electron density leads to an easier oxidation by 20 and 30 mV for the 1st and 40 and 60 mV for the 2nd wave for **6** and **7**, respectively, versus

3b. A similar shift was observed for the ferrocene-bridged NCN pincer complexes $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-NCNH})_2$ and $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-4-NCN-1-PdCl})_2$, respectively, in which the NCN pincer unit is directly attached to the cyclopentadienyl group [10,11].

The difference of the Fe(II)/Fe(III) redox couples (ΔE_0 , Table 1) can be used to determine the stability of the mixed-valence Fe(II)–Fe(III) species, relative to the iso-valent $\text{Fe(II)–Fe(II)/Fe(III)–Fe(III)}$ systems [9a,12]. The values of the conproportionation constant $K_c \text{Fe}_2$ for **3a**, **3b**, **6** and **7** are of similar order of magnitude and are within the range as found for biferrocene (Table 1) [10]. This indicates that the introduction of either a palladium(II) or platinum(II) ion does not destabilize the mixed-valence Fe(II)–Fe(III) species as it has been the case for other tetrametallic biferrocene complexes [4,9a].

Despite the generation of the oxidized species **3**, **5** and **6** at the electrode surface on the electrochemical time scale, we were not able to isolate mixed valence species. It was found that, for example, chemical oxidation led to color changes, but, however, always resulted in decomposition of the appropriate oxidized systems.

The peak potential differences found for complexes **3**, **5** and **6** are typical for oligo- and poly-ferrocenyl alkyne linkages, i.e. $[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{C}\equiv\text{CR})]_2$ ($\text{R} = \text{SiMe}_3$, Fc) and $[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_4(\eta^2\text{-C}\equiv\text{CR})\text{Co}_2(\text{CO})_6)]_2$ [4].

3. Conclusion

An efficient synthesis of tetrametallic biferrocene-based complexes of structural type $[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-C}\equiv\text{C-NCN-MBr})]_2$ ($\text{M} = \text{Pd}$, Pt ; $\text{NCN} = [\text{C}_6\text{H}_2(\text{CH}_2\text{N-Me}_2)_2\text{-2,6}]^-$) by the oxidative addition of $[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{C}\equiv\text{C-NCN-Br})]_2$ to the palladium(0) and platinum(0) sources $[\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3]$ and $[\text{Pt}(\text{tol})_2(\text{SEt}_2)]_2$ is described. In these organometallic molecules different multiple electronegative transition metals are linked by linear conjugated organic bridging units.

As it could be shown ethynyl biferrocenyl units can function as excellent modular bridging entities in the construction of complexes of higher nuclearity. Thus obtained complexes possess reasonable stability in the solid state. The ferrocenyl redox centers act independently of each other, however, the biferrocene linking unit does not modulate the redox chemistry of the end-capped NCN-MBr ($\text{M} = \text{Pd}$, Pt) building blocks. The peak potential differences ΔE for all new synthesized compounds result in only a rough measure of electron communication.

4. Experimental

4.1. 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. Isopropylamine and triethylamine were 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 $^{13}\text{C}\{^1\text{H}\}$ NMR at 62.86 MHz) in the Fourier transform mode. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane 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 argon at 25 °C. Platinum wires served as working and as counter electrode. A saturated calomel electrode served as reference electrode. For ease of comparison, all 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 ($E_0 = 0.00$ V). Electrolyte solutions were prepared from freshly distilled tetrahydrofuran or dichloromethane and $[n\text{-Bu}_4\text{N}]\text{PF}_6$ (dried in oil-pump vacuum at 120 °C, $c = 0.1$ M). The respective organometallic complexes were added at $c = 1.0$ mM. Cyclic voltammograms were recorded at a scan rate of 100 mV s^{-1} using 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 Galenkamp MFB 595 010M melting point apparatus. Microanalyses were performed by the Department of Organic Chemistry at Chemnitz, Technical University. ESI-TOF mass spectra were recorded with a Mariner ESI-TOF mass spectrometer (Applied Biosystems) operating in the positive-ion mode using dichloromethane as solvent.

4.2. General remarks

$[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{C}\equiv\text{CH})]_2$ (**1**) [9], $\text{I-1-C}_6\text{H}_3(\text{CH}_2\text{-NMe}_2)_2\text{-3,5}$ (**2a**) [12], $\text{I-1-C}_6\text{H}_2(\text{CH}_2\text{NMe}_2)_2\text{-3,5-Br-4}$ (**2b**) [7], $[\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3]$ (**4**) [8], and $[\text{Pt}(\text{4-tol})_2(\text{SEt}_2)]_2$ (**5**) [13,14] were prepared following published procedures. All other chemicals were purchased from commercial suppliers and were used without any further purification.

4.3. Synthesis

4.3.1. Synthesis of $[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{C}\equiv\text{C-I-NCNH})]_2$ (**3a**)

Compound **1** (500 mg, 1.20 mmol) and **2** (540 mg, 1.70 mmol) were dissolved in 50 mL of diisopropylamine and 70 mg (0.10 mmol, 4.0 mol%) of $[(\text{Ph}_3\text{P})_2\text{PdCl}_2]$ and 20 mg (0.10 mmol, 4.0 mol%) of $[\text{CuI}]$ were added. After stirring the reaction mixture for 4 h at reflux, all volatiles were removed (oil-pump vacuum). The reddish-brown residue was then dissolved in 100 mL of diethyl ether and extracted with a mixture of 100 mL of H_2O and 5 mL of 4 M HCl. The aqueous phase was 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

MgSO_4 , filtered through a pad of Celite, evaporated in oil-pump vacuum and purified by column chromatography (Silica gel, 7×5 cm) with diethyl ether and tetrahydrofuran (ratio 1:1). The first yellow-orange band was discarded. With methanol a 2nd fraction could be eluted. Evaporation of the solvent in oil-pump vacuum afforded **3a** as a brown solid. Yield: 320 mg (0.40 mmol, 47% based on **2a**).

M.p.: 64 °C. IR (KBr): $[\text{cm}^{-1}]$ 2212 (w) $[\nu_{\text{C}\equiv\text{C}}]$. ^1H NMR (CDCl_3): $[\delta]$ 2.25 (s, 24H, NMe_2), 3.40 (s, 8H, CH_2N), 4.04 (pt, $J_{\text{HH}} = 1.9$ Hz, 4H, C_5H_4), 4.22 (pt, $J_{\text{HH}} = 1.9$ Hz, 4H, C_5H_4), 4.26 (pt, $J_{\text{HH}} = 1.9$ Hz, 4H, C_5H_4), 4.43 (pt, $J_{\text{HH}} = 1.9$ Hz, 4H, C_5H_4), 7.20 (t, $^4J_{\text{HH}} = 1.4$ Hz, 2H, C_6H_3), 7.29 (d, $^4J_{\text{HH}} = 1.4$ Hz, 4H, C_6H_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $[\delta]$ 45.3 (NCH_3), 63.9 (NCH_2), 65.9 ($^i\text{C}/\text{C}_5\text{H}_4$), 68.1 ($\text{CH}/\text{C}_5\text{H}_4$), 69.8 ($\text{CH}/\text{C}_5\text{H}_4$), 70.0 ($\text{CH}/\text{C}_5\text{H}_4$), 72.3 ($\text{CH}/\text{C}_5\text{H}_4$), 84.1 ($^i\text{C}/\text{C}_5\text{H}_4$), 86.0 ($\text{FcC}\equiv\text{C}$), 87.8 ($\text{FcC}\equiv\text{C}$), 123.7 ($^i\text{C}/\text{C}_6\text{H}_3$), 129.0 ($\text{CH}/\text{C}_6\text{H}_3$), 130.6 ($\text{CH}/\text{C}_6\text{H}_3$), 138.9 ($^i\text{C}/\text{C}_6\text{H}_3$). Anal. Calc. for $\text{C}_{48}\text{H}_{54}\text{Fe}_2\text{N}_4$ (798.66): C, 72.19; H, 6.82; N, 7.03. Found: C, 72.25; H, 6.67; N, 6.98%.

4.3.2. Synthesis of $[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{C}\equiv\text{C-4-NCN-I-Br})]_2$ (**3b**)

Compound **3b** was prepared according to the procedure described for **3a**, using 380 mg (0.91 mmol) of **1**, 500 mg (1.26 mmol) of **2b**, 50 mg (0.07 mmol, 4.0 mol%) of $[(\text{Ph}_3\text{P})_2\text{PdCl}_2]$ and 14 mg (0.07 mmol, 4.0 mol%) of $[\text{CuI}]$ in 50 mL of triethylamine. The title compound was purified by column chromatography over alumina using diethyl ether as eluent for the 1st band and a mixture of diethyl ether–tetrahydrofuran in the ratio of 3:2 for the 2nd fraction. After evaporation of the solvents, **3b** was obtained as a red-brown solid. Yield: 305 mg (0.32 mmol, 51% based on **2b**).

M.p.: 79 °C. IR (KBr): $[\text{cm}^{-1}]$ 2213 (w) $[\nu_{\text{C}\equiv\text{C}}]$. ^1H NMR (CDCl_3): $[\delta]$ 2.34 (s, 24H, NMe_2), 3.53 (s, 8H, CH_2N), 4.06 (pt, $J_{\text{HH}} = 1.8$ Hz, 4H, C_5H_4), 4.22 (pt, $J_{\text{HH}} = 1.8$ Hz, 4H, C_5H_4), 4.26 (pt, $J_{\text{HH}} = 1.8$ Hz, 4H, C_5H_4), 4.42 (pt, $J_{\text{HH}} = 1.8$ Hz, 4H, C_5H_4), 7.40 (s, 4H, C_6H_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $[\delta]$ 45.6 (NCH_3), 63.7 (NCH_2), 65.7 ($^i\text{C}/\text{C}_5\text{H}_4$), 67.9 ($\text{CH}/\text{C}_5\text{H}_4$), 69.7 ($\text{CH}/\text{C}_5\text{H}_4$), 70.0 ($\text{CH}/\text{C}_5\text{H}_4$), 72.4 ($\text{CH}/\text{C}_5\text{H}_4$), 84.1 ($^i\text{C}/\text{C}_5\text{H}_4$), 85.4 ($\text{C}\equiv\text{C}$), 88.8 ($\text{C}\equiv\text{C}$), 122.6 ($^i\text{C}/\text{C}_6\text{H}_2$), 126.0 ($^i\text{CBr}/\text{C}_6\text{H}_2$), 131.7 ($\text{CH}/\text{C}_6\text{H}_2$), 138.7 ($^i\text{C}/\text{C}_6\text{H}_2$). Anal. Calc. for $\text{C}_{48}\text{H}_{52}\text{Br}_2\text{Fe}_2\text{N}_4$ (956.45): C, 60.28; H, 5.48; N, 5.86. Found: C, 59.93; H, 5.29; N, 5.76%.

4.3.3. Synthesis of $[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{C}\equiv\text{C-4-NCN-I-PdBr})]_2$ (**6**)

60 mg (0.063 mmol) of **3b** and 60 mg (0.058 mmol) of **4** in 15 mL of benzene were stirred for 18 h at 25 °C. Afterwards, 20 mL of tetrahydrofuran were added and the reaction mixture was stirred for 4 h at room temperature. All volatiles were removed in oil-pump vacuum, the greenish-black residue was dissolved in 20 mL of chloroform, filtered through a pad of Celite, and concentrated in oil-pump vacuum to 3 mL. *n*-Hexane (30 mL) was added, whereby an

orange solid precipitated which was washed three times with *n*-hexane (10 mL) and then with diethyl ether (10 mL) to gave **6** as an orange solid. Yield: 45 mg (0.038 mmol, 66% based on **4**).

M.p.: 142 °C (dec.). IR (KBr): [cm⁻¹] 2212 (w) [$\nu_{C\equiv C}$]. ¹H NMR (CDCl₃): [δ] 2.99 (s, 24H, N Me₂), 3.99 (s, 8H, CH₂N), 4.05 (pt, J_{HH} = 1.8 Hz, 4H, C₅H₄), 4.21 (pt, J_{HH} = 1.8 Hz, 4H, C₅H₄), 4.25 (pt, J_{HH} = 1.8 Hz, 4H, C₅H₄), 4.40 (pt, J_{HH} = 1.8 Hz, 4H, C₅H₄), 6.88 (s, 4H, C₆H₂). ¹³C{¹H} NMR (CDCl₃): [δ] 53.7 (NCH₃), 66.1 (ⁱC/C₅H₄), 68.2 (CH/C₅H₄), 69.8 (CH/C₅H₄), 70.2 (CH/C₅H₄), 72.4 (CH/C₅H₄), 74.3 (NCH₂), 84.3 (ⁱC/C₅H₄), 86.3 (C \equiv), 87.2 (C \equiv), 122.6 (CH/C₆H₂), 128.4 (ⁱC/C₆H₂), 145.0 (ⁱC/C₆H₂), 158.2 (ⁱC/C₆H₂). Anal. Calc. for C₄₈H₅₂Br₂Fe₂N₄Pd₂ · 1/2C₆H₆ (1169.29): C, 50.69; H, 4.59; N, 4.63. Found: C, 50.79; H, 4.10; N, 4.28%.

4.3.4. Synthesis of [(η^5 -C₅H₄)Fe(η^5 -C₅H₄C \equiv C-4-NCN-1-PtBr)]₂ (**7**)

100 mg (0.105 mmol) of **3b** and 95 mg (0.102 mmol) of **5** dissolved in 15 mL of toluene were stirred at reflux 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 washed twice with *n*-hexane (10 mL) and diethyl ether (10 mL) and dried in oil-pump vacuum to afford 80 mg (0.059 mmol, 58% based on **5**) of **7**.

M.p.: 159 °C (dec.). IR (KBr): [cm⁻¹] 2211 (w) [$\nu_{C\equiv C}$]. ¹H NMR (CDCl₃): [δ] 3.11 (bs, ³J_{PT}H = 34.8 Hz, 24H, N Me₂), 4.01 (bs, 8H, CH₂N), 4.04 (bs, 4H, C₅H₄), 4.25 (bs, 8H, C₅H₄), 4.41 (pt, J_{HH} = 1.8 Hz, 4H, C₅H₄), 6.91 (s, 4H, C₆H₂). ESI-TOF MS [m/z (rel. int.)] 1346.2 (15) [M⁺], 1043.1 (10) [M⁺-C₂H₄BrPt], 858.1 (100) [M⁺-C₂NCNPtBr+H]. Anal. Calc. for C₄₈H₅₂Br₂Fe₂-N₄Pt₂ (1346.61): C, 42.81; H, 3.81; N, 4.16. Found: C, 42.60; H, 3.91; N, 4.38%.

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References

- [1] (a) For example C.T. Chen, K.S. Suslick, *Coord. Chem. Rev.* 128 (1993) 293; (b) F. Paul, C. Lapinte, *Coord. Chem. Rev.* 178–180 (1998) 431; (c) C. Hortholary, C. Coudret, *J. Org. Chem.* 68 (2003) 2167; (d) S. Rigaut, J. Perruchon, L. Le Pichon, D. Touchard, P.H. Dixneuf, *J. Organomet. Chem.* 67 (2003) 37; (e) T.Y. Dong, M.C. Lin, M.Y.N. Chiang, J.Y. Wu, *Organometallics* 23 (2004) 3921; (f) A. Avrim, M. Ratner, in: *Molecular Electronics: Science and Technology*, The New Academy of Science and Technology, New York, 1998; (g) J.M. Tour, *Acc. Chem. Res.* 33 (2000) 791; (h) D. Astruc, *Acc. Chem. Res.* 30 (1997) 383; (i) J.P. Launay, *Chem. Soc. Rev.* 30 (2001) 386; (j) M.D. Ward, *Chem. Soc. Rev.* 24 (1995) 121; (k) J.A. McCleverty, M.D. Ward, *Acc. Chem. Res.* 31 (1998) 842; (l) H. Lang, *Angew. Chem., Int. Ed. Engl.* 33 (1994) 547; (m) U.H.F. Bunz, *Angew. Chem., Int. Ed. Engl.* 35 (1996) 969; (n) T.M. Swager, *Acc. Chem. Res.* 31 (1998) 201; (o) M. Mayor, C. von Hänisch, H.B. Weber, J. Reichert, D. Beckmann, *Angew. Chem., Int. Ed. Engl.* 41 (2002) 1183; (p) J.W. Ying, D.R. Sobraningh, G.L. Xu, A.E. Kaifer, T. Ren, *Chem. Commun.* (2005) 357.
- [2] (a) For example see P.D. Beer, P.A. Gale, G.Z. Chen, *Coord. Chem. Rev.* 185–186 (1999) 3; (b) O.B. Sutcliffe, M.R. Bryce, A.S. Batsanov, *J. Organomet. Chem.* 656 (2002) 211; (c) P.D. Beer, E. Hayes, *J. Coord. Chem. Rev.* 240 (2003) 167; (d) J. Razumiene, A. Vilkanauskite, V. Gureviciene, V. Laurinavicius, N.V. Roznyatovskaya, Y.V. Ageeva, M.D. Reshetova, A.D. Ryabov, *J. Organomet. Chem.* 668 (2003) 83; (e) M.J. Moloto, S.M. Nelana, R.M. Moutloali, I.A. Guzei, J. Darkwa, *J. Organomet. Chem.* 689 (2003) 387.
- [3] (a) W. Kaim, W. Bruns, S. Kohlmann, M. Krejciak, *Inorg. Chim. Acta* 229 (1995) 143; (b) M.H. Delville, *Inorg. Chim. Acta* 281 (1999) 1; (c) I.R. Farrell, F. Hartl, S. Zalis, T. Mahabiersing, *J. Chem. Soc. Dalton Trans.* (2000) 4323; (d) R.D.A. Hudson, *J. Organomet. Chem.* 637–639 (2001) 47; (e) A.S. Abd-El-Aziz, E.K. Todd, *Coord. Chem. Rev.* 246 (2003) 3; (f) I. Fratoddi, C. Battocchio, A. Furlani, P. Mataloni, G. Polzonetti, M.V. Russo, *J. Organomet. Chem.* 674 (2003) 10.
- [4] (a) D.M. Hendrickson, S.M. Oh, T.Y. Dong, T. Kambara, M.J. Cohn, M.F. Moore, *Comm. Inorg. Chem.* 4 (1985) 329; (b) M.H. Delville, F. Robert, P. Gouzerh, J. Linares, K. Boukheddaden, F. Varret, D. Astruc, *J. Organomet. Chem.* 451 (1993) C10; (c) T.Y. Dong, M.J. Cohn, D.N. Hendrickson, C.G. Pierpont, *J. Am. Chem. Soc.* 107 (1985) 4478; (d) T.Y. Dong, D.N. Hendrickson, C.G. Pierpont, M.F. Moore, *J. Am. Chem. Soc.* 108 (1986) 963; (e) L.A. Hore, C.J. McAdam, J.L. Kerr, N.W. Duffy, B.H. Robinson, J. Simpson, *Organometallics* 19 (2000) 5039; (f) Y. Mori, T. Kasai, T. Takesada, H. Komatsu, H. Yamazaki, M. Haga, *Chem. Lett.* (2001) 996; (g) T.Y. Dong, B.R. Huang, S.M. Peng, G.H. Lee, M.Y. Chiang, *J. Organomet. Chem.* 659 (2002) 125; (h) T.Y. Dong, C.K. Chang, S.H. Lee, L.L. Lai, M.Y.N. Chiang, K. Lin, *J. Organometallics* 16 (1997) 5816; (i) T.Y. Dong, L.S. Chang, I.M. Tseng, S.J. Huang, *Langmuir* 20 (2004) 4471; (j) T.Y. Dong, H.W. Shih, L.S. Chang, *Langmuir* 20 (2004) 9340.
- [5] K. Sonogashira, Y. Tohda, N. Hagihara, *Tetrahedron Lett.* 50 (1975) 4467.
- [6] (a) D.M. Grove, G. van Koten, J.N. Louwen, J.G. Noltes, A.L. Spek, H.J.C. Ubbels, *J. Am. Chem. Soc.* 104 (1982) 6609; (b) M.C. Lagunas, R.A. Gossage, A.L. Spek, G. van Koten, *Organometallics* 17 (1998) 731; (c) S. Back, M. Lutz, A.L. Spek, H. Lang, G. van Koten, *J. Organomet. Chem.* 620 (2001) 227.
- [7] G. Rodríguez, M. Albrecht, J. Schoenmaker, A. Ford, M. Lutz, A.L. Spek, G. van Koten, *J. Am. Chem. Soc.* 124 (2002) 5127.
- [8] S. Komiya, *Synthesis of Organometallic Compounds*, Wiley, Winchester, UK, 1997.
- [9] (a) M.C.B. Colbert, D. Hodgson, J. Lewis, P.R. Raithby, N. Long, *J. Polyhedron* 14 (1995) 2759; (b) N.J. Long, A.J. Martin, R. Vilar, A.J.P. White, D.J. Williams, M. Younus, *Organometallics* 18 (1999) 4261.

- [10] N. Comire, U.T. Müller-Westerhoff, W.E. Geiger, J. Organomet. Chem. 637–639 (2001) 823.
- [11] S. Köcher, G.P.M. van Klink, G. van Koten, H. Lang, J. Organomet. Chem. 684 (2003) 230.
- [12] (a) D.E. Richardson, H. Taube, Coord. Chem. Rev. 60 (1984) 107;
(b) C. Creutz, Prog. Inorg. Chem. 30 (1983) 73.
- [13] H.P. Dijkstra, M.D. Meijer, J. Patel, R. Kreiter, G.P.M. van Klink, M. Lutz, A.L. Spek, A.J. Canty, G. van Koten, Organometallics 20 (2001) 3157.
- [14] (a) B.R. Steele, K. Vrieze, Transition Met. Chem. 2 (1977) 140;
(b) A.J. Canty, J. Patel, B.W. Skelton, A.J. White, J. Organomet. Chem. 599 (2000) 195.