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Imidazoline-2-ylidene metal complexes with pendant ferrocenyl substituents

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Abstract

Imidazolium and benzimidazolium salts with ferrocenylated alkyl side chains are prepared as progenitors of *N*-[(ferrocenyl)alkyl](benz)imidazoline-2-ylidene carbenes, which form metal complexes of W(0), Pd(II), and Hg(II). X-ray structures and other spectroscopic properties show that these carbene precursors and complexes are analogous to published non-ferrocenylated complexes with regard to the coordination sphere at the metal, but different in terms of steric protection of the central metal by the bulky ferrocenyl substituents and in terms of distinguishable redox potentials of the ferrocene/ferrocenium couple. © 1998 Elsevier Science S.A.

Keywords: Carbene; Ferrocene; Iron; Tungsten; Palladium; Mercury; X-ray structure

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1. Introduction

It is now well established that carbenes exist not only as unstable reactive intermediates, but can also be isolated in pure form, if the carbene carbon is part of a heterocyclic ring and/or substituted by two electron-donating moieties [1–6]. Since the first report on a stable and crystalline imidazoline-2-ylidene by Arduengo et al. [7], based on chemistry developed earlier by Wanzlick [8,9], Wanzlick and Schikora [10], Wanzlick and Schönherr [11–13] and, Schönherr and Wanzlick [14], the chemical properties of these nucleophilic carbenes have been investigated within the recent years by Arduengo et al. [15–19], Herrmann et al. [20–26], Öfele et al. [27], Kuhn et al. [28–32], Enders et al. [33–36], Teles et al. [37] and others [38–44]. In addition, a number of theoretical studies concerning the stability and electronic structure [45–48] have been published.

The nucleophilicity of these imidazoline-2-ylidenes is now well documented [10,8,9,11,14,12,13,15–23,27,24–26,28–34,37,35,36,38–44], resulting in stable Lewis acid–base complexes with electrophiles from almost all groups of the periodic table. From an application-oriented point of view, the high stability of such metal carbene complexes and their compatibility with various oxidation states of the metal is of practical interest in the design of new transition metal catalysts for Heck coupling reactions and hydrosilylations [20–23,27,24–26,34]. Furthermore, the free carbenes themselves are very active catalysts for benzoin-type C–C-coupling reactions [9,11,33,37].

Recent work by Herrmann et al. [20–26], Öfele et al. [27], Enders et al. [33–36] and Teles et al. [37] shows the significance of steric and electronic effects of the 1,3-substituents of the imidazoline-2-ylidenes with respect to their catalytic activity and selectivity. Whereas up to now only organic substituents have been varied, either to optimize the catalyst's performance, or to introduce remote functional groups to immobilize the catalyst on a solid support, we were interested in the steric and electronic influences exhibited by ferrocenyl substituents. Sterically, the ferrocenyl moiety represents a quite bulky group with unique spatial requirements

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due to its cylindrical shape, and electronically, the powerful donor capacity of ferrocene [49] might in principle be of advantage for an additional stabilization of the electron-deficient carbene moiety.

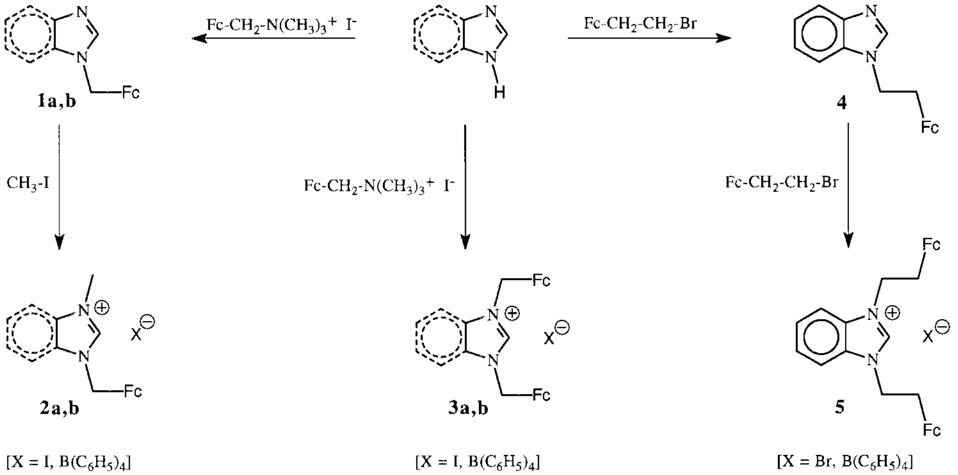
Here we report on the synthesis, spectroscopic properties, and X-ray structures of 1,3-ferrocenyl-alkyl substituted imidazoline-2-ylidene metal complexes. In this work, the ferrocenyl groups are attached to the heterocyclic carbene by means of an alkyl (-CH_2- and -CH_2-CH_2-) spacer. This rules out any major electronic interaction with the imidazoline-2-ylidene, but the flexibility of the alkyl spacer will minimize any disadvantageous steric congestion in the carbene–metal complexes. The electronic influence of the metallocenyl groups, directly connected to the imidazoline without spacer, will be addressed in a forthcoming paper [50].

2. Results and discussion

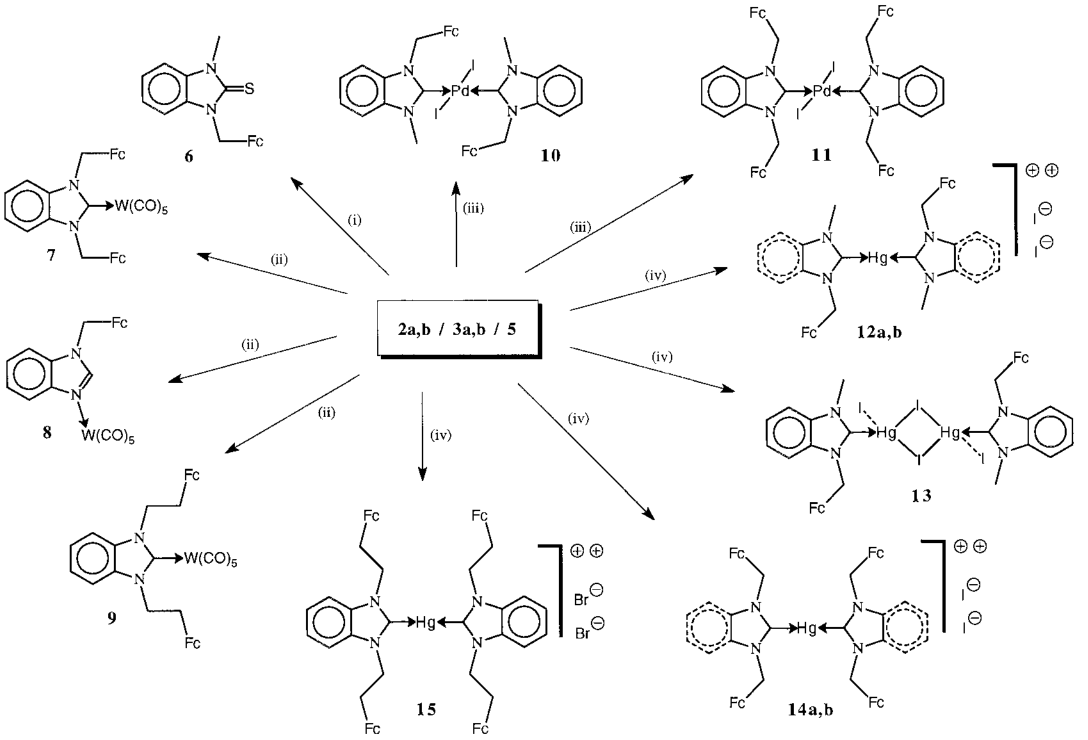
2.1. Synthesis

The ferrocenylmethylation of imidazole or benzimidazole (Scheme 1) is most easily accomplished by reaction of the corresponding heterocycle with (trimethylammonium) methylferrocene iodide, which has long been known to be an excellent electrophile due to the good leaving group property of trimethylamine [51–56]. In this manner, mono- or di-substitution can be achieved, affording **1a,b**, **3a,b** and the unsymmetrical **2a,b** after quaternization with methyl iodide. In general, imidazole derivatives **1b**, **2b**, **3b** are obtained in inferior yield in comparison to benzimidazole compounds **1a**, **2a**, **3a**. Therefore most of the following chemistry (metal complexes, see below) was performed with the benzimidazolium salts. The ethylene-spacered ferrocenylbenzimidazoles **4** and **5** were prepared starting from (2-bromoethyl)ferrocene, which was synthesized from (2-hydroxyethyl)ferrocene [57–62], obtained by an improved route from monolithioferrocene and ethylene oxide [63]. For electrochemical investigations of the ferrocenylbenzimidazolium salts (where iodide and bromide oxidations overlap with the ferrocene/ferrocenium couple) in comparison to carbene complexes derived therefrom the corresponding tetraphenylborates were obtained by anion exchange with sodium tetraphenylborate in methanol solution.

Azolium salts **2a,b**, **3a**, **3b**, **5** were subjected to some typical carbene derivatizations (Scheme 2). Deprotonation of **2a** with *n*-BuLi and subsequent thionation with elemental sulfur affords thiourea **6**, in analogy to published work on other carbenes [22,35,36,64–67]. The carbenes derived from **3a** or **5** form with $W(CO)_5THF$ the corresponding complexes **7** and **9**, similar to the reaction of other nucleophilic carbenes with metal carbonyls [20–23,27,24–26]. In the case of **3a** the reaction does not only yield complex **7**, but also nucleophilic substitution products **8** (which is simply the tungstenpentacarbonyl-complexed **1a**) and 2,3-dihydro-2-butyl-1,3-*bis*(ferrocenylmethyl) benzimidazole in low yield. The formation of **8** is explainable by the electrophilic property of **3a** in analogy to trimethylammonium methylferrocene iodide [51–56] with neutral **1a** as leaving group, which is complexed by $W(CO)_5THF$ in a simple ligand exchange reaction. The 2,3-dihydro-2-butyl benzimidazole side product arises from nucleophilic addition (versus deprotonation), similar to the behavior of azolium salts with sterically unhindered alcoholates [10,8,9,11,14,12,13,33,34,37,35,36]. As expected, reaction of ethylene-spacered **5** with $W(CO)_5THF$ yielded complex **9** with no such unwanted nucleophilic addition product analogous to **8**, because no α-ferrocenyl-α-azolium system is present.



Scheme 1. Synthesis of compounds **1a,b**–**5** (Fc = ferrocenyl; a = benzimidazole, b = imidazole, respectively).



Scheme 2. Synthesis of compounds **6**–**15** (Fc = ferrocenyl; a = benzimidazole, b = imidazole, respectively). Reagents: (i) *n*-BuLi, S_{el}; (ii) BuLi, $W(CO)_5 \cdot THF$; (iii) $Pd(OAc)_2$; (iv) $Hg(OAc)_2$.

Starting from carbene progenitors **2a,b**, **3a,b**, **5** and Pd(II) or Hg(II) acetates the corresponding metal carbene complexes **10**–**15** were synthesized by in situ deprotonation with acetate as base and subsequent complex formation (Scheme 2). This one pot reaction (direct metal complex synthesis without prior carbene formation) is based on work by Schönnher and Wanzlick [14] and, Wanzlick and Schönnher [12,13], who isolated and structurally characterized the first Hg(II) complex of a nucleophilic carbene [14] as early as 1968. For four-coordinated Pd(II) complexes this method works only in the presence of iodide as stabilizing additional ligand. The iodide is usually (and most conveniently) supplied 'internally' as the counter ion of the azolium salt, but it can also be added from an 'external' source of an excess of NaI in the reaction mixture [34]. As expected, Hg(II) complexes **12a,b**, **14a,b** and **15** with two carbene ligands per metal are ionic and hence very polar and only slightly soluble compounds, but complex **13** with stochiometrically one carbene moiety per metal unit (which is the precursor complex of **12a** and which could therefore be isolated in only low yield) is a dimer with covalently bonded halogeno ligands and therefore much more soluble (see Section 2.2 for structural details).

2.2. Spectroscopic and structural properties

The spectroscopic properties of the carbene precursors **2a,b**, **3a,b**, **5** are as expected and show no unusual features. For comparative purposes with the following carbene complexes, crystal structure analyses of **2a** (Fig. 1, Table 1) and **3b** (Fig. 2, Table 1) were performed. Besides the steric requirements of the ferrocenyl substituents, the interest in these and the following structures focuses on the bonding situation at the carbene carbon in terms of bond lengths and angles. As has been amply demonstrated by other workers [15–23,27,24–26,28–34,37,35,36], the C–N bond lengths of the carbene carbon are almost identical for imidazolium salts, imidazoline and imidazolidine carbenes, and the various metal complexes derived therefrom. Not surprisingly, the carbene carbon in compounds **2a**, **3b**, **6**, **7**, **11**, **13** has very similar bond lengths in comparison to these published results (for relevant data see Figs. 1–6). The N–C–N angles in azolium salts **2a** (109.9(8)°) and **3b** (109.0(3)°) compare well with those of reported imidazolium carbene precursors (e.g., 108.7(4)° for 1,3-dimesitylimidazolium [15]) and, as will be seen in the following, this angle decreases in the corresponding carbene complexes in accord with published work on other imidazoline-2-ylidene metal complexes [15–23,27,24–26,28–34,37,35,36].

Products **6**–**9** are simple carbene derivatives, which were mainly synthesized to prove that these ferrocenyl(benz)imidazoline-2-ylidenes can be prepared from the corresponding azolium salts **2a**, **3a** and **5** by sequential deprotonation and reaction with the respective electrophiles. Thiourea **6** shows spectroscopic prop-

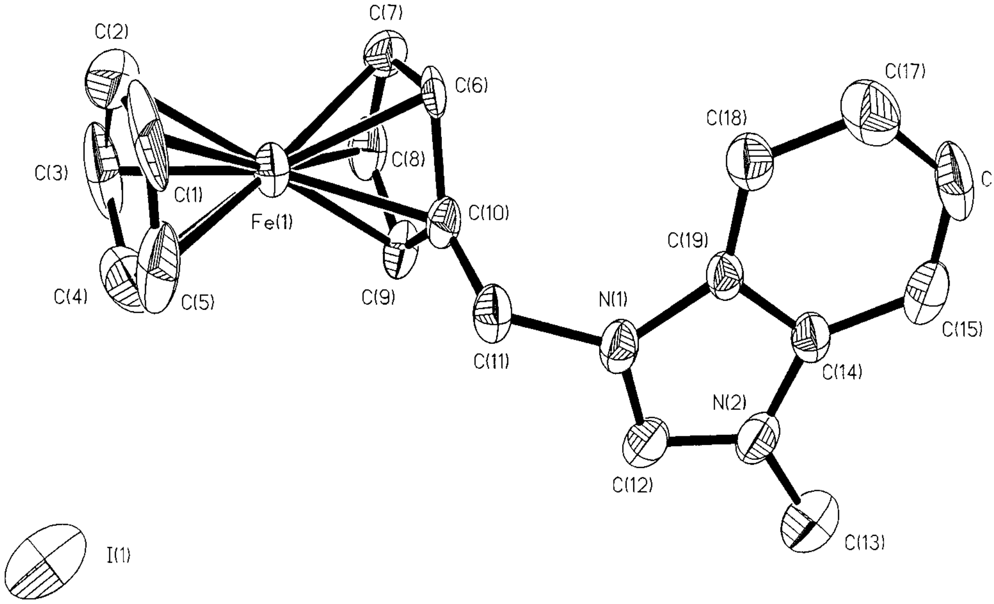


Fig. 1. Molecular structure of **2a**. Solvent molecules H_2O, CH_3OH and hydrogens are omitted for clarity. Selected bond lengths (pm) and angles (°): C(12)–N(1) = 133.9(9), C(12)–N(2) = 133.5(9), N(1)–C(19) = 139.8(9), N(2)–C(14) = 137.8(10), C(14)–C(19) = 139.4(10); N(1)–C(12)–N(2) = 109.9(8), C(12)–N(1)–C(19) = 108.4(6), C(12)–N(2)–C(14) = 108.5(7), N(1)–C(11)–C(10) = 110.3(6).

erties in solution which are in line with the expectations and the solid state structure (Fig. 3) is very similar—with regard to the thioimidazoline backbone–to a recently published example [22]. Similarly, tungsten pentacarbonyl complex **7** has unexceptional NMR spectroscopic properties and the X-ray structure (Fig. 4) compares well with analogous complexes reported by Herrmann et al. [20–22] and Kuhn et al. [32].

Whereas the NMR spectroscopic parameters of compounds **6**–**9** can be interpreted in a straightforward manner, this is not the case for palladium and mercury complexes **10**–**15**. Problems arise because these compounds show only very limited solubility in common organic solvents and the mercury complexes **12**–**15** tend to decompose in solution (compare experimental part). In addition, for palladium compounds different diastereoisomers are possible (*cis–trans*, *trans–syn*, *trans–anti*), depending on the substitution pattern of the carbene ligand (unsymmtric or symmetric) and the steric bulk of the N-substituents of the (benz)imidazole [25,34].

Due to these difficulties the most useful information can be obtained from mass spectroscopy and from X-ray structures. The identities of palladium complexes **10** and **11** are clearly established by observation of the molecular ions ($m/z = 1020$ and 1388, respectively) as the base peaks (100%) in the FAB-mass spectra. The more polar and less soluble ionic mercury complexes **12**–**15** require electrospray ionization to obtain useful data. In general, the highest signal observed is the monocation corresponding to the formula mass of the complexes minus one halogenide (Fig. 5).

Suitable single crystals for X-ray analysis could be obtained for compounds **11** and **13**. The palladium complex **11** (Fig. 6) shows the expected square-planar coordination sphere at the Pd atom with *trans*-carbene ligands. Due to the steric bulk of the ferrocenyl groups they are arranged in an alternating up–down fashion, thereby minimizing steric congestion. These substituents (and the iodo and benzimidazole ligands) are symmetrically related to each other by an inversion center located on the central Pd atom. The benzimidazole rings are twisted against the square-planar coordination sphere by 85.17(23)°, similar as in other imidazoline-2-ylidene complexes [15–23,27,24–26,33,34, 37,35,36]. The bond length Pd–$C_{carbene}$ of 202.4(7) pm is in the usually observed range (195–207 pm) for palladium carbene complexes [25,34].

As mentioned earlier, the first *bis*-imidazolin-2-ylidene Hg(II) complex was isolated by Schönherr and Wanzlick [14] and, Wanzlick and Schönherr [12,13] and structurally characterized [14,68], showing the expected linear coordination with a $C_{carbene}$–Hg distance of 206(1) pm. Most likely all of the analogous *bis*-carbene complexes **12a,b**, **14a,b**, and **15** in this work will have a similar structure with regard to the coordination at mercury. All attempts to obtain suitable single crystals for these complexes failed, except for the dimeric mono-carbene complex 13 (Fig. 7). The molecule exists as a dimer with *trans*-carbene ligands and with bridging (Hg(1)–I(2) = 289.42(7) pm) and non-bridging (Hg(1)–I(1) = 270.91(8) pm) iodine ligands. An inversion center located in the center of the central Hg_2I_2-rhombus

Table 1
Crystal data and structure refinement for **2a**, **3b**, **6**, **7**, **11**, **13**

	2a	**3b**	**6**	**7**	**11**	**13**
Molecular formula	$C_{19}H_{19}FeIN_2 \cdot H_2O \cdot (CH_3OH)_{1/4}$	$C_{25}H_{25}Fe_2IN_2$	$C_{19}H_{18}FeN_2S$	$C_{34}H_{26}Fe_2N_2O_5W$	$C_{58}H_{52}Fe_4I_2N_4Pd \cdot (CH_2Cl_2)_4$	$C_{38}H_{36}Fe_2Hg_2I_4N_4 \cdot (C_3H_7NO)_2$
Formula weight	484.14	592.07	362.26	838.12	1728.34	1715.38
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	C2/c (No. 15)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (pm)	1837.5 (4)	1496.1 (1)	810.7 (1)	1230.4(2)	1123.7(2)	751.40(10)
b (pm)	1649.8 (3)	1519.1 (2)	1153.3 (2)	945.0(2)	1146.8(2)	1178.20(10)
c (pm)	1246.6 (2)	1034.5 (1)	1776.6 (3)	2605.5(11)	1484.0(2)	1522.1(2)
α (°)	90	90	90	90	71.13(1)	79.570(10)
β (°)	91.06 (2)	95.51 (1)	97.34 (1)	92.73(3)	78.00(1)	77.220(10)
γ (°)	90	90	90	90	65.15(1)	72.670(10)(2)
Volume (nm^3)	3.7784 (12)	2.3403 (4)	1.6475 (4)	3.026(2)	1.6363(5)	1.2448(3)
Z	8	4	4	4	1	1
Temperature (K)	203	293	213	213	213	213
Density, calc. ($Mg\ m^{-3}$)	1.702	1.680	1.461	1.840	1.754	2.288
Absorption coefficient (mm^{-1})	2.442	2.573	1.042	4.784	2.447	9.240
$F(000)$	1924	1176	752	1640	852	796
Color, habit	yellow platelet	orange prism	yellow prism	Yellow block	Orange prism	Yellow prism
Crystal size (mm)	$0.20 \times 0.14 \times 0.10$	$0.70 \times 0.60 \times 0.25$	$0.50 \times 0.40 \times 0.35$	$0.20 \times 0.10 \times 0.10$	$0.30 \times 0.30 \times 0.25$	$0.40 \times 0.20 \times 0.10$
θ range for data collection (°)	2.22 to 20.99	2.66 to 24.00	3.09 to 23.50	2.66 to 20.49	3.04 to 23.40	3.12 to 23.97
Index ranges	$-1 \leq h \leq 16$, $-1 \leq k \leq 16$, $-12 \leq l \leq 12$	$-17 \leq h \leq 17$, $-18 \leq k \leq 1$, $-1 \leq l \leq 10$	$-9 \leq h \leq 0$, $0 \leq k \leq 13$, $-19 \leq l \leq 20$	$-1 \leq h \leq 11$, $-1 \leq k \leq 9$, $-26 \leq l \leq 23$	$-1 \leq h \leq 11$, $-11 \leq k \leq 12$, $-15 \leq l \leq 16$	$-1 \leq h \leq 7$, $-12 \leq k \leq 12$, $-16 \leq l \leq 16$
Reflections collected	2283	4409	2412	2819	4196	3503
Independent reflections	1864 ($R_{int} = 0.0322$)	3428 ($R_{int} = 0.0179$)	2390 ($R_{int} = 0.0125$)	2641 ($R_{int} = 0.0316$)	3927 ($R_{int} = 0.0310$)	3194 ($R_{int} = 0.0384$)
Reflections with $I > 2\sigma(I)$	1328	2863	2092	1924	3410	2703
Absorption correction	ψ-scan	ψ-scan	ψ-scan	ψ-scan	ψ-scan	ψ-scan
Max. and min. transmission	0.991 and 0.771	0.995 and 0.522	0.928 and 0.841	0.882 and 0.847	0.959 and 0.790	1.000 and 0.592
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1705/0/231	3274/0/275	2292/0/209	2457/0/297	3776/0/385	3064/0/274
Goodness-of-fit on F^2	1.055	1.086	1.070	1.034	1.030	1.044
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0410$, $wR_2 = 0.0705$	$R_1 = 0.0317$, $wR_2 = 0.0752$	$R_1 = 0.0298$, $wR_2 = 0.0741$	$R_1 = 0.0429$, $wR_2 = 0.0706$	$R_1 = 0.0430$, $wR_2 = 0.1145$	$R_1 = 0.0315$, $wR_2 = 0.0724$
R indices (all data)	$R_1 = 0.0776$, $wR_2 = 0.1018$	$R_1 = 0.0416$, $wR_2 = 0.0822$	$R_1 = 0.0373$, $wR_2 = 0.0809$	$R_1 = 0.0764$, $wR_2 = 0.0808$	$R_1 = 0.0518$, $wR_2 = 0.1249$	$R_1 = 0.0432$, $wR_2 = 0.0779$
Largest diff. peak and hole ($e\ nm^{-1}$)	554 and −471	347 and −657	234 and −294	768 and −749	1711 and −689	895 and −1279

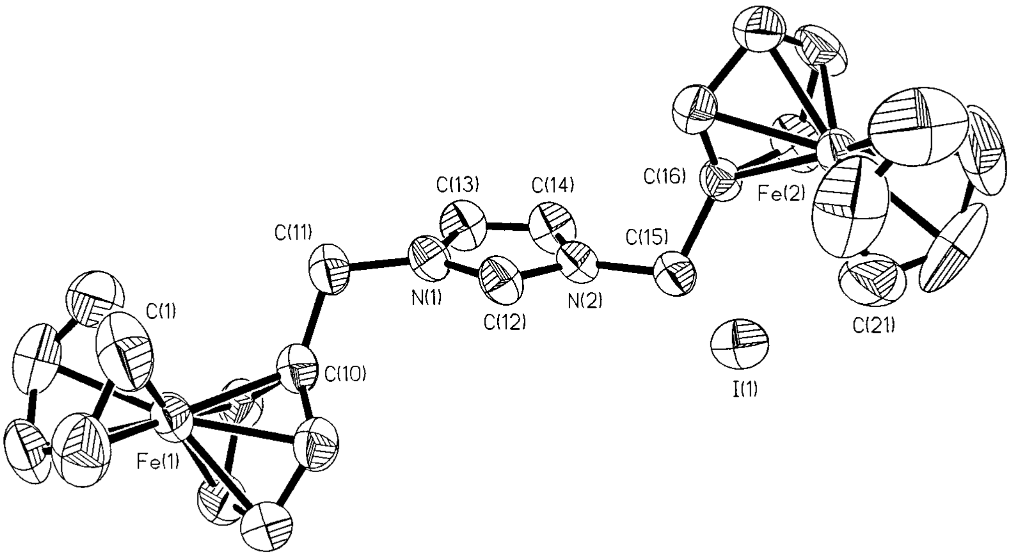


Fig. 2. Molecular structure of **3b**. Hydrogen atoms are omitted for clarity. Cyclopentadienyl carbons of ferrocene 1 are C(1)–C(10) and for ferrocene 2 C(16)–C(25), respectively. Selected bond lengths (pm) and angles (°): C(12)–N(1) = 131.7(5), C(12)–N(2) = 132.9(5), N(1)–C(13) = 137.7(5), N(2)–C(14) = 137.5(5), C(13)–C(14) = 133.8(6); N(1)–C(12)–N(2) = 109.0(3), C(12)–N(1)–C(13) = 108.1(3), C(12)–N(2)–C(14) = 108.5(3), N(1)–C(11)–C(10) = 112.7(3), N(2)–C(15)–C(16) = 110.8(3).

(Hg(1)–I(2)–Hg(1a) = 86.18(2)°) interconverts the iodine and carbene ligands. The coordination sphere of mercury is more or less tetrahedral, with some distortions (C(12)–Hg(1)–I(1) = 131.4(2)°, I(2)–Hg(1)–I(2a) = 93.82(2)°). The metal–carbene bond length Hg(1)–C(12) of 214.7(7) pm is elongated in comparison to Wanzlick's *bis*-carbene complex ($C_{carbene}$–Hg = 206(1) pm [14,68]), but shorter than in the comparable mercury dimer $[(C_6H_5)_3P(Cp)HgI_2]_2$, C–Hg = 229(2) pm [69,70], due to partial double bonding in **13**.

The presence of ferrocenyl substituents in compounds **1**–**15** allows in principle electrochemical measurements of the ferrocene/ferrocenium (Fc/Fc^+) couple. Unfortunately, if iodine or bromine ligands are present, no clean cyclovoltammograms were obtained due to signal overlapping; therefore only the non-halogen containing azolium salts and metal complexes could be investigated electrochemically. Because in this series of compounds the ferrocenyl electrophor is separated by a non-conjugated saturated alkyl spacer, we did not

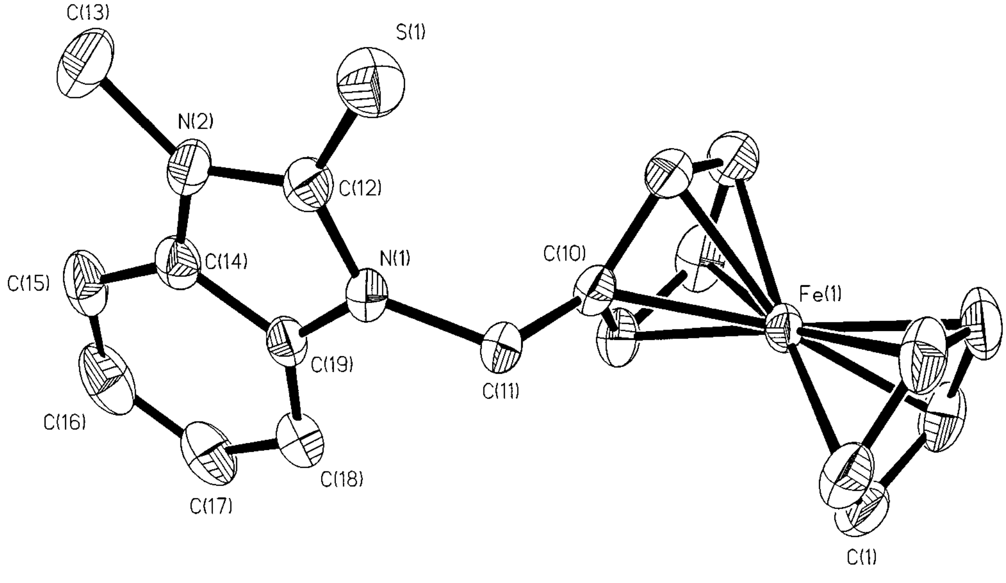


Fig. 3. Molecular structure of **6**. Hydrogen atoms are omitted for clarity. Cp carbons of ferrocene 1 are C(1)–C(10). Selected bond lengths (pm) and angles (°): C(12)–S(1) = 165.9(3), C(12)–N(1) = 136.5(3), C(12)–N(2) = 136.5(3), N(1)–C(19) = 139.1(3), N(2)–C(14) = 137.8(4), C(14)–C(19) = 139.9(3); N(1)–C(12)–N(2) = 106.6(2), C(12)–N(1)–C(19) = 109.9(2), C(12)–N(2)–C(14) = 110.3(2), N(1)–C(11)–C(10) = 111.4(2).

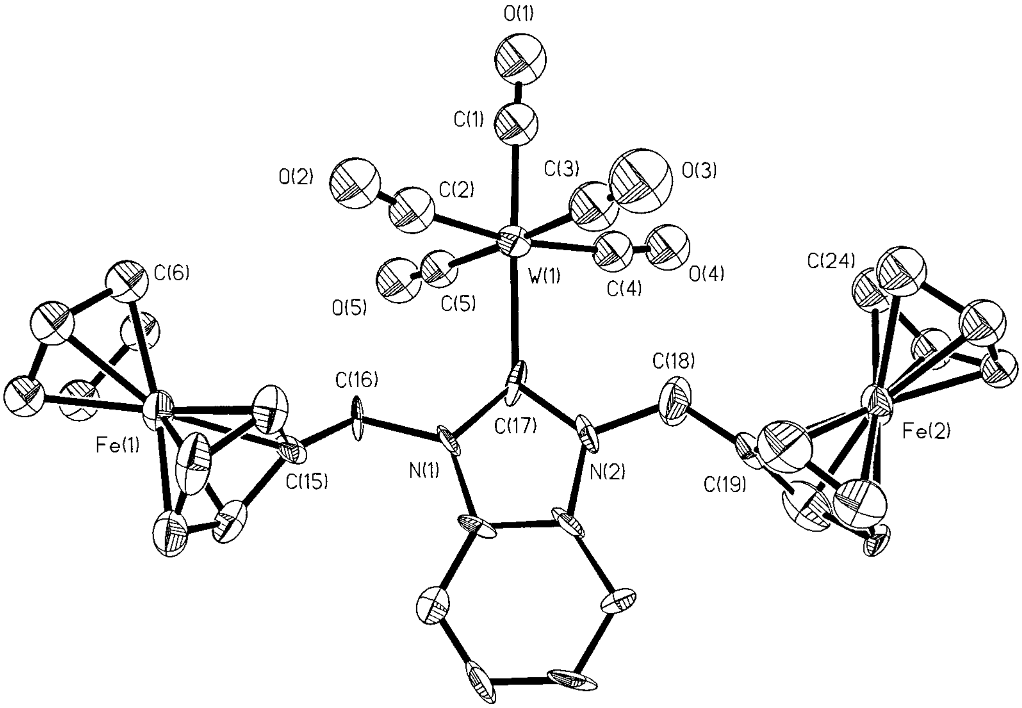


Fig. 4. Molecular structure of **7**. Hydrogen atoms are omitted for clarity. Cyclopentadienyl carbons of ferrocene 1 are C(6)–C(15) and for ferrocene 2 C(19)–C(28), respectively. Phenylene carbons of benzimidazoline are C(29)–C(34). Selected bond lengths (pm) and angles (°): C(17)–W(1) = 226.4(14), C(17)–N(1) = 135.0(2), C(17)–N(2) = 135.7(14), N(1)–C(30) = 138(2), N(2)–C(29) = 139(2), C(29)–C(30) = 139(2); N(1)–C(17)–N(2) = 103.3(11), C(17)–N(1)–C(30) = 112.4(10), C(17)–N(2)–C(29) = 113.4(11), N(1)–C(16)–C(15) = 113.4(9), N(2)–C(18)–C(19) = 116.3(11).

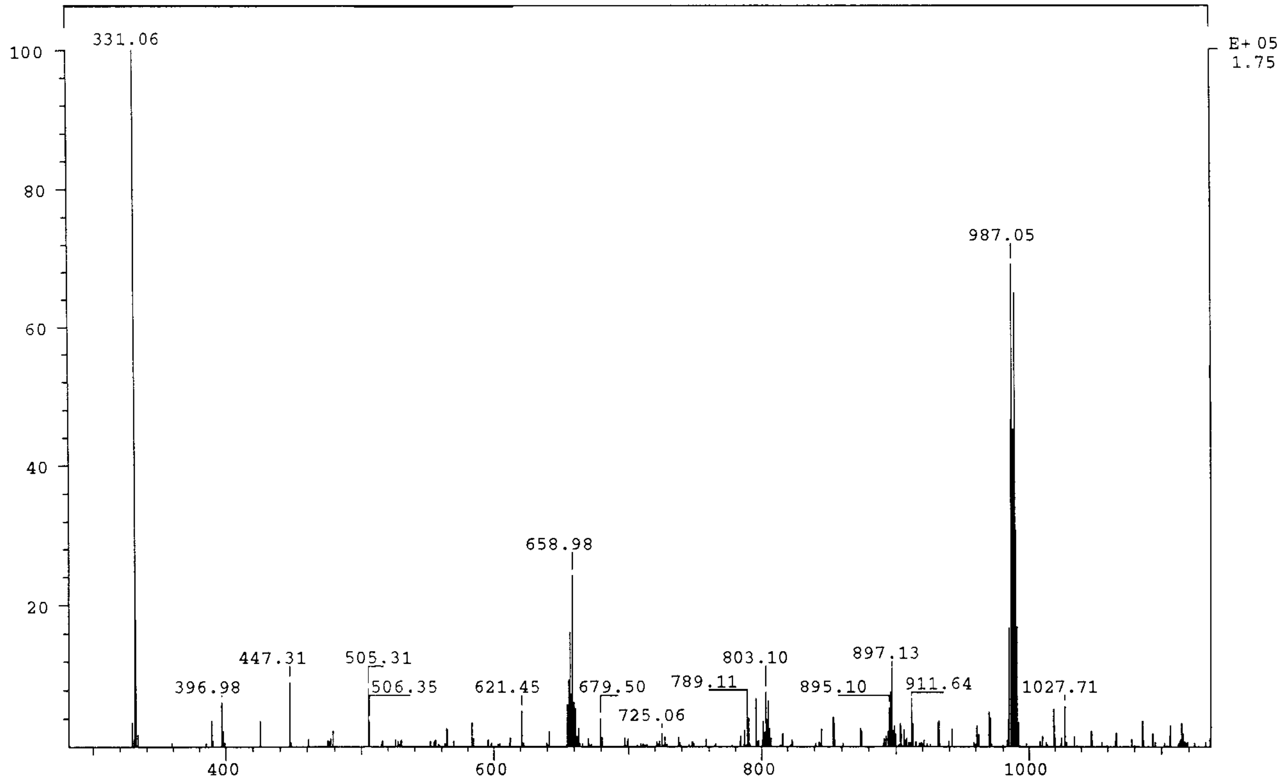


Fig. 5. (+)ESI mass spectrum of **12a** ($C_{38}H_{36}N_4Fe_2HgI_2$; M_r = 1114.82 g/mole); m/z = 987(75%) corresponds to M^+ minus one iodine.

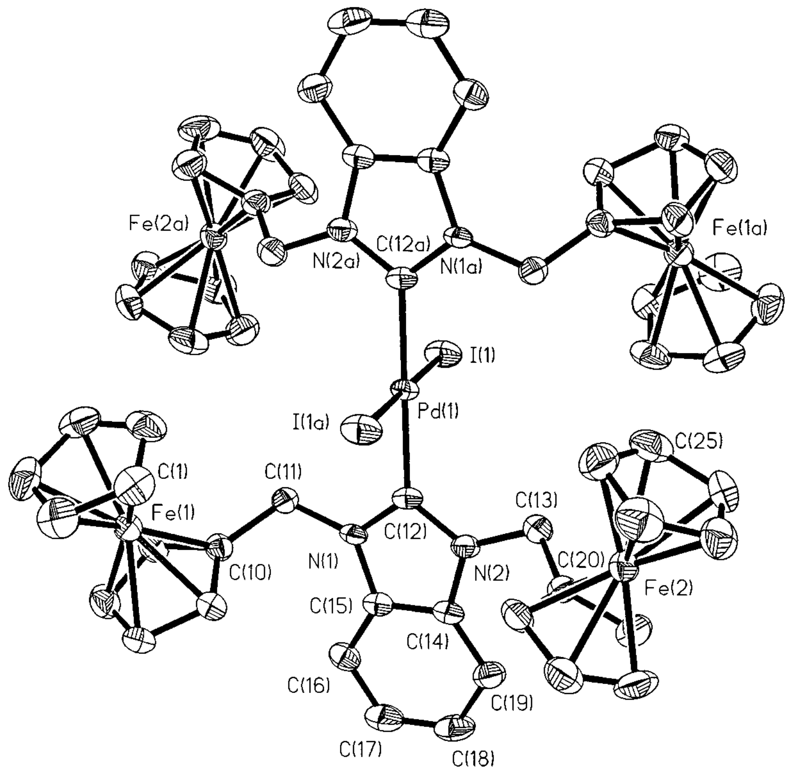


Fig. 6. Molecular structure of **11**. Hydrogen atoms and dichloromethane molecules are omitted for clarity. Cyclopentadienyl carbons of ferrocene 1 are C(1)–C(10) and for ferrocene 2 C(20)–C(29), respectively. Selected bond lengths (pm) and angles (°): C(12)–Pd(1) = 202.4(7), Pd(1)–I(1) = 259.05(7), C(12)–N(1) = 135.5(9), C(12)–N(2) = 135.4(9), N(1)–C(15) = 140.1(9), N(2)–C(14) = 139.5(9), C(14)–C(15) = 137.4(10); C(12)–Pd(1)–C(12a) = 180.0, C(12)–Pd(1)–I(1) = 88.6(2), N(1)–C(12)–N(2) = 106.0(6), C(12)–N(1)–C(15) = 110.3(5), C(12)–N(2)–C(14) = 110.9(6), N(1)–C(11)–C(10) = 113.0(5), N(2)–C(13)–C(20) = 112.9(6).

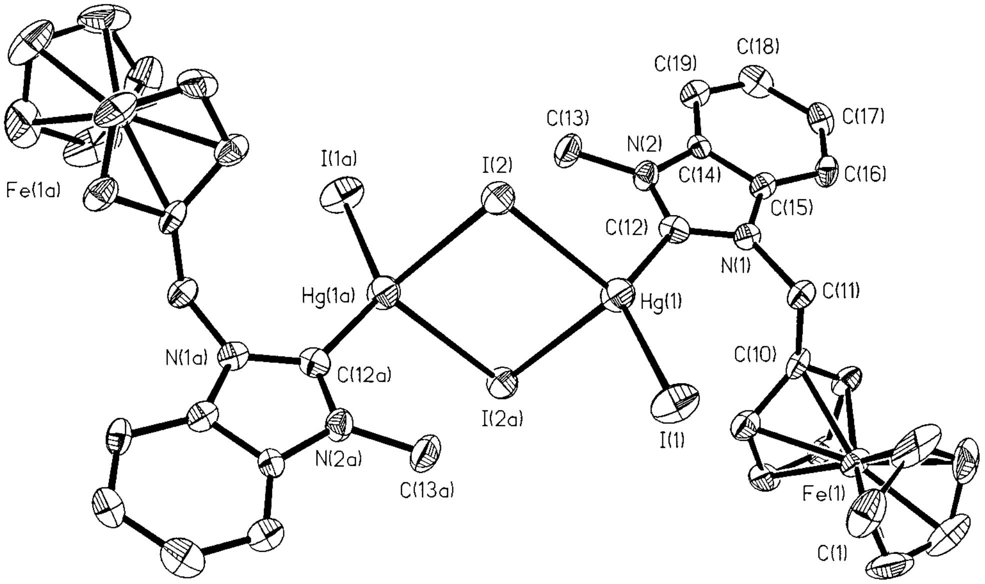


Fig. 7. Molecular structure of **13**. Hydrogen atoms and DMF molecules are omitted for clarity. Cyclopentadienyl carbons of ferrocene 1 are C(1)–C(10). Selected bond lengths (pm) and angles (°): C(12)–Hg(1) = 214.7(7), Hg(1)–I(1) = 270.91(8), Hg(1)–I(2) = 289.42(7), C(12)–N(1) = 134.8(10), C(12)–N(2) = 133.8(10), N(1)–C(15) = 139.5(10), N(2)–C(14) = 140.3(9), C(14)–C(15) = 138.5(10); I(2)–Hg(1)–I(2a) = 93.82(2), C(12)–Hg(1)–I(1) = 131.4(2), C(12)–Hg(1)–I(2) = 111.4(2), C(12)–Hg(1)–I(2a) = 104.1(2), N(1)–C(12)–N(2) = 106.4(6), C(12)–N(1)–C(15) = 110.5(6), C(12)–N(2)–C(14) = 111.3(6), N(1)–C(11)–C(10) = 112.6(6).

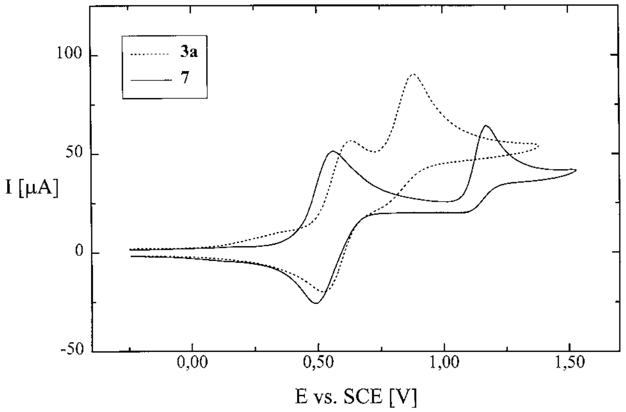


Fig. 8. Cyclic voltammetry of **3a** and **7**.

expect any major changes in comparison to the parent FcH/FcH$^+$ couple. Surprisingly, significant relative shifts in the half-wave potential from -120 mV to $+130$ mV were observed. Tetraphenylborates **2a**, **3a**, **5** show values of 0.57, 0.58, 0.45 V, and carbene derivatives **6**, **7**, **9** values of 0.47, 0.53, 0.43 V, respectively. In each case only one reversible Fc/Fc$^+$ wave is observed, irrespective of the number of ferrocenyl substituents (Fig. 8). Although no simple interpretation of these data in terms of some linear correlation can be envisaged at this point, the different electrochemical response might serve as an additional distinguishing property in this series of compounds.

3. Conclusions

A number of imidazolium and benzimidazolium salts with N,N′-alkyl(ferrocenyl) substituents has been prepared and converted to W(0), Pd(II), and Hg(II) metal carbene complexes. X-ray structures show that the bulky ferrocenyl groups effectively shield the central metal core and cyclovoltammetric measurements of the ferrocenium/ferrocene couple reveal distinguishable half-wave potentials. These carbene derivatives are the first examples of such imidazoline-2-ylenes incorporating an organometallic moiety and they might prove useful in potential applications in homogenous catalysis.

4. Experimental section

4.1. General techniques and instrumentation

Reactions of air-sensitive materials were carried out using standard Schlenk techniques and vacuum-line manipulations. Solvents were deoxygenated, purified and dried prior to use. Instrumentation: Bruker AC 200 (^{1}H, ^{13}C; ^{1}H and ^{13}C signals were referenced to internal residual solvent peaks); Nicolet 510 FT-IR (IR); Varian CH-7 (EI-MS), Finnigan MAT 95 (FAB-, ESI-MS). Melting points were determined on a Leica–Reichert VM-TG hot plate apparatus. Microanalyses were obtained from the Analytical Department of Lenzing AG, Lenzing, Austria.

Cyclic voltammetric measurements were performed at room temperature with a POS 88 Potentiostat (Bank Elektronik), using a standard three electrode apparatus, an atmosphere of purified argon, acetonitrile as solvent, a scan rate of 100 mV/sec, and 0.1 M tetrabutylammonium hexafluorophosphate ([TBA]PF$_6$) as the conducting salt. The signals were referenced to the saturated calomel electrode (SCE) by calculating the corresponding half wave potentials from cobaltocenium/cobaltocene as an internal standard versus SCE (SCE; $E_{1/2} = -0.93$ V).

*4.2. X-ray structure determinations of **2a**, **3b**, **6**, **7**, **11**, **13***

A Siemens P4 diffractometer with graphite-monochromatized Mo–Kα radiation ($\lambda = 71.073$ pm) was used for data collection. Crystal data, data collection, and refinement parameters of **2a**, **3b**, **6**, **7**, **11**, **13** are summarized in Table 1. The unit cells were determined by the automatic indexing of 25 centered reflections and confirmed by examination of the axial photographs. Data were measured via ω-scan and corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography [71] and an empirical absorption correction [72,73] was made. The structures were solved by direct methods, SHELXS86 [74], and refined by a full matrix least-squares procedure using SHELXL-93 [75]. All non-hydrogen atoms were refined with anisotropic displacement parameters (Tables 2–7), except for **7** due to insufficient data/parameter ratio (compare note in Table 5). Hydrogen atoms were placed in calculated positions. The authors have deposited atomic coordinates for structures **2a**, **3b**, **6**, **7**, **11**, **13** at the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, Lensfield Road, Cambridge, CB2 1EW, UK.

*4.3. N-(ferrocenylmethyl) benzimidazole **1a** and n-(ferrocenylmethyl)imidazole **1b***

N-(ferroenylmethyl)benzimidazole is a known compound [76,77], but no physical or spectroscopic data have been published, therefore we describe its preparation and properties in detail. A mixture of 2 g (5.2 mmol) [1 g (2.6 mmol), respectively] (ferrocenylmethyl)trimethyl ammonium iodide [51–56] and 0.766 g (6.5 mmol) benzimidazole [0.22 g (3.2

Table 2
Atomic coordinates (10^4) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for **2a**

	x	y	z	U_{eq}
Fe(1)	3999 (1)	1331 (1)	− 147 (1)	28 (1)
I(1)	3452 (1)	4425 (1)	1842 (1)	67 (1)
N(1)	3467 (4)	2550 (4)	− 3214 (5)	30 (2)
N(2)	3914 (4)	3212 (4)	− 4573 (5)	37 (2)
C(1)	3150 (7)	1157 (12)	842 (8)	77 (4)
C(2)	3769 (11)	740 (6)	1230 (9)	76 (4)
C(3)	4296 (6)	1310 (11)	1410 (6)	68 (3)
C(4)	4025 (7)	2055 (7)	1161 (8)	56 (3)
C(5)	3343 (8)	1984 (8)	804 (7)	60 (3)
C(6)	3752 (4)	843 (5)	− 1612 (5)	28 (2)
C(7)	4401 (5)	510 (5)	− 1200 (6)	37 (2)
C(8)	4911 (4)	1131 (6)	− 1022 (6)	37 (2)
C(9)	4575 (4)	1871 (5)	− 1318 (6)	31 (2)
C(10)	3854 (4)	1705 (5)	− 1691 (5)	26 (2)
C(11)	3316 (4)	2317 (5)	− 2079 (6)	30 (2)
C(12)	3825 (5)	3218 (5)	− 3513 (7)	36 (2)
C(13)	4292 (5)	3841 (5)	− 5172 (7)	58 (3)
C(14)	3599 (4)	2518 (5)	− 4985 (6)	30 (2)
C(15)	3542 (5)	2228 (6)	− 6042 (6)	40 (2)
C(16)	3168 (5)	1503 (6)	− 6156 (6)	50 (3)
C(17)	2870 (5)	1080 (5)	− 5306 (7)	49 (3)
C(18)	2939 (4)	1375 (5)	− 4270 (6)	34 (2)
C(19)	3303 (4)	2093 (5)	− 4131 (6)	25 (2)
O(1)	3931 (5)	4020 (5)	− 958 (7)	132 (3)
C(20)	4822 (10)	4602 (13)	− 2030 (15)	116 (8)
O(20)	4822 (10)	4602 (13)	− 2030 (15)	116 (8)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

mmol) imidazole respectively] in 10 ml DMF was refluxed for 2 h. The brown solution was hydrolized with 100 ml H_2O and extracted with five portions of ether. The combined organic layers were washed with three portions of H_2O, dried with Na_2SO_4, and evaporated to dryness on a rotary evaporator, yielding 1.321 g (4.2 mmol, 77.3%) **1a** and 0.39 g (1.5 mmol, 54%) **1b**, respectively.

Data for **1a**: yellow crystals, m.p. 119–122°C. Anal. Found: C, 68.42; H, 5.13 $C_{18}H_{16}FeN_2$. Calcd.: C, 68.38; H, 5.10%. IR(KBr): cm^{-1} 3077w, 2927w, 1489s, 1456m, 1443s, 1348w, 1283m, 1263s, 1157w, 1101s, 1038m, 1026s, 1003w, 739s, 509s, 488s. MS(EI, 70 eV): m/z(%) 316(100) (M^+), 199(61) ($FcCH_2$). ^1H NMR (DMSO-d_6): d 4.15 (m, 2H, Cp_{subst}), 4.16 (s, 5H, $Cp_{unsubst}$), 4.23 (m, 2H, Cp_{subst}), 5.05 (s, 2H, CH_2), 7.25–7.88 (m, 5H, benzimidazole). ^{13}C NMR (DMSO-d_6): d 44.7 (CH_2), 68.77 ($Cp_{unsubst}$ and Cp_{subst}), 82.04 (C(1) of Cp_{subst}); 109.7, 120.34, 122.0, 122.8 (benzimidazole).

Data for **1b**: yellow crystals, m.p. 79–81°C. Anal. Found: C, 63.24; H, 5.32 $C_{14}H_{14}FeN_2$. Calcd.: C, 63.19; H, 5.30%. IR(KBr): cm^{-1} 3106w, 2963w, 1510m, 1283m, 1261s, 1236m, 1225m, 1103s, 1080s, 1040s, 1028s, 804s, 744m, 667w, 617w, 503s, 482s. MS(EI, 70 eV): m/z(%) 266(100) (M^+), 199(96) ($FcCH_2$), 188.5(44) (M^+–Cp), 121(83) (FeCp). ^1H NMR ($CDCl_3$): d 4.13 (m, 7H, Cp_{subst} and $Cp_{unsubst}$), 4.16 (m, 2H, Cp_{subst}), 4.82 (s, 2H, CH_2), 6.87 (s, 1H, imidazole), 6.99 (s, 1H, imidazole), 7.44 (s, 1H, imidazole). ^{13}C NMR (DMSO-d_6): d 44.7 (CH_2), 68.5 (Cp_{subst}), 68.7 (Cp_{subst}), 68.73 ($Cp_{unsubst}$), 80.0 (C(1) of Cp_{subst}); 118.8, 129.1, 136.6 (imidazole).

*4.4. 1-(Ferrocenylmethyl)-3-methyl-benzimidazolium iodide and tetraphenylborate **2a** and 1-(ferrocenylmethyl)-3-methyl-imidazolium iodide **2b***

0.2 g (0.6 mmol) of **1a** was dissolved in 1 ml (16 mmol) methyl iodide and refluxed for 2 h. The resulting precipitate of crude **2a**-iodide was filtered off and washed with small portions of ether until the ether fractions were colorless. Yield: 0.285 g (0.6 mmol, 98%). Conversion of the **2a**-iodide into **2a**-tetraphenylborate: a solution of the iodide (0.108 g, 0.24 mmol) in methanol was added to a solution of $NaB(C_6H_5)_4$ (0.12 g, 0.35 mmol) in methanol, the resulting **2a**-tetraphenylborate was filtered off, washed with three portions of

Table 3
Atomic coordinates (10^4) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for **3b**

	x	y	z	U_{eq}
Fe(1)	− 3812 (1)	3758 (1)	3382 (1)	48 (1)
Fe(2)	2549 (1)	3800 (1)	1555 (1)	40 (1)
I(1)	722 (1)	7244 (1)	218 (1)	66 (1)
N(1)	− 1101 (2)	4857 (2)	3493 (3)	42 (1)
N(2)	12 (2)	4989 (2)	2333 (3)	39 (1)
C(1)	− 3526 (4)	2573 (4)	4205 (7)	84 (2)
C(2)	− 4356 (4)	2535 (4)	3445 (6)	80 (2)
C(3)	− 4928 (3)	3148 (4)	3935 (6)	74 (2)
C(4)	− 4458 (4)	3562 (4)	5003 (5)	80 (2)
C(5)	− 3599 (4)	3204 (5)	5160 (6)	87 (2)
C(6)	− 2913 (3)	3943 (3)	2046 (4)	54 (1)
C(7)	− 3795 (3)	4139 (4)	1493 (4)	64 (1)
C(8)	− 4141 (3)	4816 (3)	2216 (5)	62 (1)
C(9)	− 3483 (3)	5054 (3)	3237 (4)	50 (1)
C(10)	− 2720 (2)	4502 (3)	3134 (4)	44 (1)
C(11)	− 1891 (3)	4478 (3)	4055 (4)	48 (1)
C(12)	− 648 (3)	4462 (3)	2630 (4)	44 (1)
C(13)	− 707 (3)	5662 (3)	3775 (4)	50 (1)
C(14)	− 17 (3)	5748 (3)	3050 (4)	51 (1)
C(15)	689 (2)	4758 (3)	1438 (4)	44 (1)
C(16)	1581 (2)	4589 (2)	2172 (4)	38 (1)
C(17)	2375 (3)	5077 (3)	2089 (5)	57 (1)
C(18)	3073 (3)	4664 (3)	2929 (5)	59 (1)
C(19)	2697 (3)	3947 (3)	3505 (4)	58 (1)
C(20)	1780 (3)	3894 (3)	3062 (4)	49 (1)
C(21)	2059 (4)	3231 (7)	− 124 (7)	96 (2)
C(22)	2821 (8)	3682 (5)	− 319 (6)	113 (3)
C(23)	3507 (4)	3313 (8)	532 (10)	117 (3)
C(24)	3148 (8)	2669 (6)	1161 (8)	123 (3)
C(25)	2272 (7)	2622 (6)	778 (10)	121 (3)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4
Atomic coordinates (10^4) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for **6**

	x	y	z	U_{eq}
Fe(1)	9856 (1)	292 (1)	2921 (1)	24 (1)
S(1)	4384 (1)	2728 (1)	1569 (1)	41 (1)
N(1)	4837 (2)	396 (2)	1599 (1)	26 (1)
N(2)	3252 (2)	1029 (2)	593 (1)	30 (1)
C(1)	10165 (3)	−778 (2)	3846 (2)	38 (1)
C(2)	11721 (3)	−330 (3)	3699 (2)	42 (1)
C(3)	11638 (3)	891 (3)	3746 (2)	44 (1)
C(4)	10039 (4)	1198 (3)	3917 (2)	42 (1)
C(5)	9131 (3)	172 (3)	3979 (2)	39 (1)
C(6)	8740 (3)	−650 (2)	2030 (1)	32 (1)
C(7)	10333 (3)	−262 (3)	1884 (2)	42 (1)
C(8)	10354 (3)	963 (3)	1912 (2)	41 (1)
C(9)	8775 (3)	1347 (2)	2075 (1)	33 (1)
C(10)	7766 (3)	351 (2)	2155 (1)	25 (1)
C(11)	5994 (3)	372 (2)	2310 (1)	26 (1)
C(12)	4174 (3)	1376 (2)	1251 (1)	28 (1)
C(13)	2237 (3)	1791 (3)	69 (2)	44 (1)
C(14)	3335 (3)	−157 (2)	517 (1)	29 (1)
C(15)	2623 (3)	−907 (3)	−46 (2)	40 (1)
C(16)	2964 (4)	−2071 (3)	60 (2)	49 (1)
C(17)	3954 (4)	−2484 (3)	706 (2)	45 (1)
C(18)	4650 (3)	−1741 (2)	1270 (2)	34 (1)
C(19)	4345 (3)	−570 (2)	1158 (1)	26 (1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

methanol, and dried in vacuo, yielding 92 mg (60%) **2a**-tetraphenylborate. Analogously, **2b**-iodide was prepared from **1b** with methyl iodide in 87% yield.

Data for **2a**-iodide: yellow crystals, m.p. 116–118°C. Anal. Found: C, 49.75; H, 4.21 $C_{19}H_{19}FeIN_2$. Calcd.: C, 49.81; H, 4.18%. IR(KBr): cm^{-1} 3015w, 2969w, 1609w, 1565s, 1463s, 1432m, 1347w, 1329s, 1238m, 1105s, 1013s, 1003w, 828s, 812m, 783w, 764s, 501s, 482m. MS(FAB): m/z(%) 331(100) (M^+ of cation). ^1H NMR ($CDCl_3$): d 4.19 (s, 3H, CH_3), 4.21 (m, 2H, Cp_{subst}), 4.29 (s, 5H, $Cp_{unsubst}$), 4.58 (m, 2H, Cp_{subst}), 5.61 (s, 2H, CH_2), 7.63–10.9 (m, 5H, benzimidazole). ^{13}C NMR (DMSO-d_6): d 33.4 (CH_3), 46.4 (CH_2), 68.9 ($Cp_{unsubst}$), 69.0 (Cp_{subst}), 69.6 (Cp_{subst}), 80.0 (C(1) of Cp_{subst}); 113.6, 113.8, 126.6, 130.5, 131.8, 141.9 (benzimidazole). X-ray structure (Tables 1 and 2; Fig. 1): single crystals were obtained from dichloromethane.

Data for **2a**-tetraphenylborate: yellow crystals, m.p. 165–167°C. Anal. Found: C, 79.37; H, 6.07. $C_{43}H_{39}FeBN_2$. Calcd.: C, 79.40; H, 6.04%. IR(KBr): cm^{-1} 3069m, 3056m, 2983w, 1564s, 1479s, 1427m, 1109w, 1030m, 1009w, 852m, 825m, 816m, 744s, 733s, 708s, 615m, 603s, 497m, 492m, 482m. MS(FAB): m/z(%) 331(100) (M^+ of cation). ^1H NMR (CD_3CN): d 3.80 (s, 3H, CH_3), 4.26 (m, 2H, Cp_{subst}), 4.27 (s, 5H, $Cp_{unsubst}$), 4.43 (m, 2H, Cp_{subst}), 5.28 (s, 2H, CH_2), 6.79 − 8.32 (m, 25H, benzimidazole and tetraphenylborate). ^{13}C NMR (CD_3CN): d 34.7 (CH_3), 48.6 (CH_2), 70.6 ($Cp_{unsubst}$), 71.1 (Cp_{subst}), 71.3 (Cp_{subst}), 80.1 (C(1) of Cp_{subst}); 114.8, 114.9, 118.9, 123.4, 127.1, 127.2, 127.2, 127.3, 128.4, 128.5, 137.3, 142.0 (benzimidazole and tetraphenylborate). CV (CH_3CN; 20°C) [V]: 0.57.

Data for **2b**-iodide: yellow crystals, m.p. 145–148°C. Anal. Found: C, 44.20; H, 4.18. $C_{15}H_{17}FeIN_2$. Calcd.: C,44.15; H, 4.20%. IR(KBr): cm^{-1} 1570s, 1238m, 1157s, 1105s, 1040s, 1028m, 1001s, 828s, 773m, 621s, 503s, 484s. MS(FAB): m/z(%) 281(100) (M^+ of cation). ^1H NMR (DMSO-d_6): d 3.80 (s, 3H, CH_3),

Table 5
Atomic coordinates (10^4) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for **7**

	x	y	z	U_{eq}
W(1)	10128 (1)	7082 (1)	3117 (1)	32 (1)
Fe(1)	5439 (2)	9156 (2)	3284 (1)	33 (1)
Fe(2)	12228 (1)	2654 (2)	4601 (1)	37 (1)
O(1)	11757 (8)	8654 (11)	2427 (4)	71 (3)
O(2)	9019 (8)	10003 (12)	3361 (4)	58 (3)
O(3)	11629 (9)	7790 (14)	4100 (4)	92 (4)
O(4)	11749 (8)	4638 (11)	2837 (4)	60 (3)
O(5)	8704 (8)	6551 (10)	2081 (4)	60 (3)
N(1)	7887 (8)	5738 (11)	3567 (4)	23 (3)
N(2)	9267 (8)	4587 (12)	3860 (4)	35 (3)
C(1)	11140 (11)	8143 (17)	2707 (5)	50(4)
C(2)	9355 (12)	8910 (17)	3270 (5)	51 (4)
C(3)	11078 (12)	7479 (16)	3740 (6)	58 (5)
C(4)	11100 (12)	5456 (16)	2945 (5)	46 (4)
C(5)	9208 (10)	6709 (14)	2458 (5)	39 (4)
C(6)	6120 (11)	10669 (15)	2847 (5)	43 (4)
C(7)	5182 (12)	11194 (14)	3080 (5)	44 (4)
C(8)	4293 (10)	10408 (15)	2923 (5)	39 (4)
C(9)	4636 (11)	9358 (15)	2585 (5)	42 (4)
C(10)	5764 (11)	9523 (15)	2534 (5)	38 (4)
C(11)	6537 (11)	8672 (15)	3866 (5)	33 (4)
C(12)	5511 (14)	9087 (17)	4061 (5)	47 (4)
C(13)	4709 (12)	8183 (19)	3857 (6)	49 (4)
C(14)	5219 (11)	7224 (15)	3546 (5)	35 (4)
C(15)	6351 (10)	7472 (14)	3544 (5)	30 (4)
C(16)	7179 (10)	6686 (13)	3244 (4)	28 (4)
C(17)	8987 (12)	5719 (14)	3562 (4)	28 (4)
C(18)	10390 (12)	4014 (18)	3904 (6)	64 (5)
C(19)	10680 (9)	3183 (15)	4372 (5)	28 (4)
C(20)	10944 (13)	3725 (19)	4858 (7)	61 (5)
C(21)	11179 (13)	2650 (25)	5190 (6)	62 (6)
C(22)	11144 (12)	1351 (20)	4933 (8)	61 (6)
C(23)	10831 (12)	1666 (18)	4400 (6)	54 (5)
C(24)	13235 (11)	3336 (15)	4060 (5)	52 (4)
C(25)	13457 (12)	4082 (17)	4506 (6)	60 (5)
C(26)	13750 (11)	3072 (17)	4900 (5)	51 (4)
C(27)	13717 (10)	1751 (14)	4684 (5)	35 (4)
C(28)	13386 (10)	1871 (16)	4152 (5)	44 (4)
C(29)	8382 (11)	3903 (16)	4058 (5)	34 (4)
C(30)	7483 (11)	4652 (15)	3859 (4)	22 (3)
C(31)	6447 (12)	4272 (16)	3967 (5)	38 (4)
C(32)	6315 (10)	3143 (17)	4280 (6)	43 (4)
C(33)	7196 (12)	2409 (15)	4494 (6)	50 (5)
C(34)	8246 (11)	2745 (16)	4388 (5)	49 (4)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. Due to the poor quality of the available single crystal only the atoms Fe(1), Fe(2), W(1), N(1), N(2), and carbons C(11)–C(23) could be refined anisotropically.

Table 6
Atomic coordinates (10^4) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for **11**

	x	y	z	U_{eq}
Pd(1)	0	0	5000	22 (1)
I(1)	1707 (1)	−2367 (1)	5673 (1)	37 (1)
Fe(1)	−490 (1)	3507 (1)	6947 (1)	29 (1)
Fe(2)	483 (1)	2271 (1)	1086 (1)	31 (1)
N(1)	1994 (5)	1015 (5)	5217 (4)	22 (1)
N(2)	2213 (6)	798 (5)	3790 (4)	25 (1)
C(1)	−2197 (8)	4211 (8)	6323 (6)	44 (2)
C(2)	−2301 (8)	5018 (8)	6895 (7)	48 (2)
C(3)	−2111 (8)	4241 (9)	7841 (6)	48 (2)
C(4)	−1879 (9)	2915 (9)	7856 (6)	46 (2)
C(5)	−1940 (8)	2913 (8)	6914 (7)	44 (2)
C(6)	965 (8)	3498 (7)	5862 (5)	36 (2)
C(7)	856 (9)	4366 (8)	6405 (6)	42 (2)
C(8)	1083 (8)	3599 (8)	7355 (6)	42 (2)
C(9)	1338 (8)	2256 (8)	7415 (5)	36 (2)
C(10)	1259 (7)	2194 (7)	6488 (5)	26 (2)
C(11)	1538 (7)	933 (7)	6221 (5)	26 (2)
C(12)	1479 (7)	676 (6)	4638 (5)	23 (2)
C(13)	1966 (8)	538 (7)	2955 (5)	32 (2)
C(14)	3210 (7)	1198 (6)	3829 (5)	25 (2)
C(15)	3077 (7)	1329 (6)	4736 (5)	24 (2)
C(16)	3921 (7)	1705 (7)	5035 (5)	30 (2)
C(17)	4926 (8)	1924 (8)	4379 (6)	41 (2)
C(18)	5062 (8)	1792 (8)	3452 (6)	41 (2)
C(19)	4205 (8)	1419 (7)	3156 (5)	34 (2)
C(20)	1752 (8)	1718 (7)	2080 (5)	32 (2)
C(21)	829 (9)	3033 (8)	2028 (5)	39 (2)
C(22)	939 (10)	3813 (8)	1084 (6)	46 (2)
C(23)	1942 (10)	3001 (10)	553 (6)	52 (2)
C(24)	2458 (8)	1684 (8)	1167 (6)	41 (2)
C(25)	−311 (9)	871 (9)	1431 (6)	45 (2)
C(26)	−1283 (8)	2110 (9)	1515 (6)	45 (2)
C(27)	−1334 (9)	3045 (9)	608 (7)	53 (2)
C(28)	−371 (9)	2358 (9)	−24 (6)	45 (2)
C(29)	241 (10)	1027 (9)	482 (6)	49 (2)
C(30)	−4160 (18)	2638 (20)	139 (11)	125 (6)
Cl(1)	−5139 (4)	3539 (4)	901 (3)	108 (1)
Cl(2)	−3768 (4)	920 (5)	612 (4)	154 (2)
C(31)	−4488 (20)	6185 (22)	3144 (35)	312 (25)
Cl(3A)	−4747 (10)	6218 (11)	3857 (4)	107 (3)
Cl(4A)	−4270 (11)	5213 (12)	2298 (10)	121 (4)
Cl(3B)	−4633 (5)	7914 (5)	2034 (5)	82 (2)
Cl(4B)	−3504 (8)	5187 (10)	2128 (7)	85 (2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. Symmetry transformations used to generate equivalent atoms: $-x, -y, -z+1$.

4.22 (m, 7H, Cp_{subst} and $Cp_{unsubst}$), 4.43 (m, 2H, Cp_{subst}), 5.15 (s, 2H, CH_2), 7.62 (s, 1H, imidazole), 7.71 (s, 1H, imidazole), 9.05 (s, 1H, imidazole). ^{13}C NMR (DMSO-d_6): d 35.9 (CH_3), 48.4 (CH_2), 68.8 ($Cp_{unsubst}$), 68.9 (Cp_{subst}), 69.0 (Cp_{subst}), 80.9 (C(1) of Cp_{subst}); 122.0, 123.6, 135.8 (imidazole).

*4.5. 1,3-Bis(ferrocenylmethyl) benzimidazolium iodide and tetraphenylborate **3a** and 1,3-bis(ferrocenylmethyl)imidazolium iodide **3b***

A mixture of 1.43 g (3.7 mmol) [2.9 g (5.2 mmol), respectively] (ferrocenylmethyl) trimethyl ammonium iodide [51–56] and 0.2 g (1.7 mmol) benzimidazole [0.16 g (2.4 mmol) imidazole, respectively] in 10 ml DMF was refluxed for 4 h. The brown solutions were hydrolized with 100 ml H_2O and extracted with five portions of ether. The combined organic layers were washed with three portions of H_2O, dried with Na_2SO_4, and evaporated to dryness on a rotary evaporator, yielding 0.582 g (0.9 mmol, 53.6%) **3a**-iodide and 0.654 g (47%) **3b**-iodide, respectively. Conversion of the **3a**-iodide into **3a**-tetraphenylborate: a solution of the iodide (0.371 g, 0.57 mmol) in methanol was added to a solution of $NaB(C_6H_5)_4$ (0.39 g, 0.87 mmol) in methanol, the resulting **3a**-tetraphenylborate was filtered off, washed with three portions of methanol, and dried in vacuo, yielding 412 mg (85%) **3a**-tetraphenylborate.

Data for **3a**-iodide: yellow crystals, m.p. 124°C, dec. Anal. Found: C, 54.18; H, 4.23. $C_{29}H_{27}Fe_2IN_2$. Calcd.: C, 54.24; H, 4.24%. IR(KBr): cm^{-1} 3064m, 1615m, 1559s, 1495s, 1458w, 1329w, 1265w, 1238s, 1171m, 1106s, 1040m, 1028m, 1001s, 820s, 750s, 501s, 482s. MS(FAB): m/z(%) 516(48) (M^+ of cation + 2H),

Table 7
Atomic coordinates (10^4) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for **13**

	x	y	z	U_{eq}
Hg(1)	−170 (1)	3827 (1)	4239 (1)	35 (1)
I(1)	−1757 (1)	4946 (1)	2770 (1)	46 (1)
I(2)	−2730 (1)	4920 (1)	5764 (1)	31 (1)
Fe(1)	3365 (2)	1884 (1)	1146 (1)	28 (1)
N(1)	1620 (8)	1091 (5)	4096 (4)	22 (2)
N(2)	1705 (9)	1459 (5)	5417 (4)	26 (2)
C(1)	1186 (15)	3114 (9)	606 (7)	51 (3)
C(2)	2838 (17)	2855 (11)	−59 (7)	57 (3)
C(3)	3402 (15)	1678 (10)	−158 (6)	54 (3)
C(4)	2133 (17)	1122 (9)	456 (7)	54 (3)
C(5)	751 (14)	2014 (13)	924 (6)	59 (3)
C(6)	3684 (11)	2551 (7)	2234 (5)	29 (2)
C(7)	5423 (12)	2334 (8)	1603 (6)	35 (2)
C(8)	5995 (12)	1112 (9)	1472 (6)	38 (2)
C(9)	4653 (12)	539 (7)	2031 (5)	30 (2)
C(10)	3194 (10)	1426 (7)	2505 (5)	23 (2)
C(11)	1440 (11)	1253 (7)	3134 (5)	27 (2)
C(12)	1177 (11)	1975 (7)	4623 (6)	25 (2)
C(13)	1524 (13)	2103 (8)	6193 (6)	35 (2)
C(14)	2455 (10)	216 (6)	5424 (5)	19 (2)
C(15)	2408 (10)	−10 (7)	4569 (5)	23 (2)
C(16)	3045 (11)	−1172 (7)	4333 (5)	27 (2)
C(17)	3740 (12)	−2059 (7)	4986 (6)	32 (2)
C(18)	3786 (12)	−1813 (7)	5859 (6)	35 (2)
C(19)	3134 (11)	−670 (7)	6089 (5)	27 (2)
O(1)	−2501 (10)	1543 (7)	7723 (5)	57 (2)
N(3)	−2473 (11)	3055 (7)	8447 (5)	41 (2)
C(20)	−3112 (14)	2592 (9)	7908 (6)	43 (2)
C(21)	−3288 (18)	4293 (9)	8624 (8)	77 (4)
C(22)	−898 (21)	2342 (11)	8885 (9)	87 (4)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. Symmetry transformations used to generate equivalent atoms: $-x, -y+1, -z+1$.

316(100) (M$^+$ of cation-FcCH$_2$). ^{1}H NMR (CDCl$_3$): d 4.19 (m, 4H, Cp$_{\text{subst}}$), 4.25 (s, 10H, Cp$_{\text{unsubst}}$), 4.54 (m, 4H, Cp$_{\text{subst}}$), 5.56 (s, 4H, CH$_2$), 7.55–10.98 (m, 5H, benzimidazole). ^{13}C NMR (DMSO-d$_6$): d 46.4 (CH$_2$), 68.9 (Cp$_{\text{unsubst}}$), 69.0 (Cp$_{\text{subst}}$), 69.5 (Cp$_{\text{subst}}$), 80.2 (C(1) of Cp$_{\text{subst}}$); 114.0, 126.8, 130.7, 140.9 (benzimidazole).

Data for **3a**-tetraphenylborate: yellow crystals, m.p. 120–122°C. Anal. Found: C, 76.15; H, 5.65. C$_{53}$H$_{47}$Fe$_2$BN$_2$. Calcd.: C, 76.29; H, 5.68%. IR(KBr): cm^{-1} 3056m, 2984w, 1580w, 1560s, 1479s, 1425m, 1238w, 1167m, 1107m, 1041w, 1030m, 1001s, 823s, 735s, 706s, 611s, 499s, 482s. MS(FAB): m/z(%) 516(100) (M$^+$ of cation). ^{1}H NMR (CDCl$_3$): d 4.38 (m, 18H, Cp$_{\text{subst}}$ and Cp$_{\text{unsubst}}$), 4.80 (s, 4H, CH$_2$), 7.07–7.74 (m, 25H, benzimidazole and tetraphenylborate). ^{13}C NMR (CDCl$_3$): d 47.7 (CH$_2$), 69.2 (Cp$_{\text{unsubst}}$), 69.4 (Cp$_{\text{subst}}$), 69.5 (Cp$_{\text{subst}}$), 78.4 (C(1) of Cp$_{\text{subst}}$); 113.3, 122.1, 126.0, 126.9, 130.7, 134.5, 136.1, 139.3 (benzimidazole and tetraphenylborate). CV (CH$_3$CN; 20°C) [V]: 0.58.

Data for **3b**-iodide: yellow crystals, m.p. 199°C, dec. Anal. Found: C, 50.76; H, 4.25. C$_{25}$H$_{25}$Fe$_2$IN$_2$. Calcd.: C, 50.71; H, 4.26%. IR(KBr): cm^{-1} 3075w, 1626m, 1557s, 1443w, 1410w, 1337w, 1238m, 1142s, 1105s, 1041s, 1028m, 1001m, 820s, 773w, 625w, 503s, 482s. MS(FAB): m/z(%) 465(100) (M$^+$ of cation). ^{1}H NMR (CDCl$_3$): d 4.29 (m, 4H, Cp$_{\text{subst}}$), 4.30 (s, 10H, Cp$_{\text{unsubst}}$), 4.51 (m, 4H, Cp$_{\text{subst}}$), 5.39 (s, 4H, CH$_2$), 7.24 (s, 2H, imidazole), 10.00 (s, 1H, imidazole). ^{13}C NMR (CDCl$_3$): d 49.9 (CH$_2$), 69.1 (Cp$_{\text{unsubst}}$), 69.6 (Cp$_{\text{subst}}$), 69.7 (Cp$_{\text{subst}}$), 78.4 (C(1) of Cp$_{\text{subst}}$); 121.0, 134.7 (imidazole). X-ray structure (Tables 1 and 3; Fig. 2): single crystals were obtained by slow diffusion of hexane into a dichloromethane solution of **3b**-iodide.

*4.6. N-(ferrocenylethyl) benzimidazole **4** and 1,3-bis(ferrocenylethyl)benzimidazolium bromide and tetraphenylborate **5***

A THF solution of 0.887 g (7.5 mmol) benzimidazole was cooled to −80°C and lithiated with 3.75 ml (7.5 mmol) *n*-butyl lithium (2.0 molar solution in hexane). After the mixture was allowed to warm to room temperature, 2 g (6.8 mmol) (2-bromoethyl)ferrocene [57–63] was added in one portion and the mixture was refluxed overnight. Aqueous work-up and chromatography (Al$_2$O$_3$, ethyl acetate as eluent) yielded 1.286 g (3.9 mmol, 57%) **4**. Conversion to **5**-bromide: a mixture of 0.794 g (2.4 mmol) **4**, 0.8 g (2.7 mmol) (2-bromoethyl)ferrocene, and 10 ml acetonitrile was refluxed for 4 days. Aqueous work-up yielded 1.33 g (2.1 mmol, 89%) **5**-bromide. Conversion of **5**-bromide to **5**-tetraphenylborate: a solution of the bromide (0.250 g, 0.40 mmol) in methanol was added to a solution of NaB(C$_6$H$_5$)$_4$ (0.21 g, 0.60 mmol) in methanol, the resulting **5**-tetraphenylborate was filtered off, washed with three portions of methanol, and dried in vacuo, yielding 310 mg (90%) **5**-tetraphenylborate.

Data for **4**: yellow crystals, m.p. 131°C. Anal. Found: C, 69.13; H, 5.51. C$_{19}$H$_{18}$FeN$_2$. Calcd.: C, 69.11; H, 5.49%. IR(KBr): cm^{-1} 3091w, 2930w, 1501s, 1458s, 1358m, 1283m, 1254m, 1223s, 1105m, 1040m, 1001w, 818m, 802m, 766w, 746s, 499m, 488m, 428w. MS(EI, 70 eV): m/z(%) 330(100) (M$^+$), 265(38) (M$^+$–Cp), 199(39) (FcCH$_2$). ^{1}H NMR (CDCl$_3$): d 2.85 (t, 2H, CH$_2$), 3.89 (m, 2H, Cp$_{\text{subst}}$), 4.05 (m, 2H, Cp$_{\text{subst}}$), 4.06 (s, 5H, Cp$_{\text{unsubst}}$), 4.21 (t, 2H, CH$_2$), 7.23–7.80 (m, 5H, benzimidazole). ^{13}C NMR (CDCl$_3$): d 30.5 (CH$_2$), 46.5 (CH$_2$), 68.0 (Cp$_{\text{subst}}$), 68.3 (Cp$_{\text{unsubst}}$), 68.5 (Cp$_{\text{subst}}$), 83.8 (C(1) of Cp$_{\text{subst}}$); 109.5, 120.4, 122.0 (benzimidazole).

Data for **5**-bromide: yellow crystals, m.p. 210°C. Anal. Found: C, 59.79; H, 4.89. C$_{31}$H$_{30}$BrFe$_2$N$_2$. Calcd.: C, 59.84; H, 4.86%. IR(KBr): cm^{-1} 3089w, 2927w, 1616m, 1489s, 1456m, 1435m, 1352w, 1175w, 1105s, 1043m, 1024m, 1001w, 821s, 810s, 762s, 484s. MS(FAB): m/z(%) 543(100) (M$^+$ of cation). ^{1}H NMR (CDCl$_3$): d 2.90 (t, 4H, CH$_2$), 4.04 (br s, 8H, Cp$_{\text{subst}}$), 4.13 (s, 10H, Cp$_{\text{unsubst}}$), 4.55 (t, 4H, CH$_2$), 7.63–9.60 (m, 5H, benzimidazole). ^{13}C NMR (CDCl$_3$): d 29.2 (CH$_2$), 47.6 (CH$_2$), 67.7 (Cp$_{\text{subst}}$), 68.3 (Cp$_{\text{subst}}$), 68.6 (Cp$_{\text{unsubst}}$), 83.2 (C(1) of Cp$_{\text{subst}}$); 113.8, 126.6, 130.9, 142.0 (benzimidazole).

Data for **5**-tetraphenylborate: yellow crystals, m.p. 192°C. Anal. Found: C, 76.71; H, 5.82. C$_{55}$H$_{50}$Fe$_2$BN$_2$. Calcd.: C, 76.68; H, 5.85%. IR(KBr): cm^{-1} 3056m, 2984w, 1557w, 1478s, 1456s, 1425m, 1107m, 1040w, 1032w, 1001m, 831m, 820s, 808m, 752s, 737s, 717s, 613s, 499s, 482s. MS(FAB): m/z(%) 543(100) (M$^+$ of cation). ^{1}H NMR (CD$_3$CN): d 2.88 (t, 4H, CH$_2$), 3.93 (m, 4H, Cp$_{\text{subst}}$), 4.06 (m, 4H, Cp$_{\text{subst}}$), 4.11 (s, 10H, Cp$_{\text{unsubst}}$), 4.39 (t, 4H, CH$_2$), 6.78–8.28 (m, 25H, benzimidazole and tetraphenylborate). ^{13}C NMR (CDCl$_3$): d 31.0 (CH$_2$), 50.0 (CH$_2$), 69.6 (Cp$_{\text{subst}}$), 70.0 (Cp$_{\text{subst}}$), 70.2 (Cp$_{\text{unsubst}}$), not observed: (C(1) of Cp$_{\text{subst}}$); 115.1, 118.9, 123.4, 127.16, 127.22, 128.4, 137.3, 142.0 (benzimidazole and tetraphenylborate). CV (CH$_3$CN; 20°C) [V]: 0.45.

*4.7. 1-(Ferrocenylmethyl)-3-methyl-benzimidazoline-2-thione **6***

A Schlenk vessel was charged with 0.19 g (0.4 mmol) **2a** and 20 ml THF. The mixture was cooled to −80°C and lithiated with *n*-butyl lithium (0.2 ml of a 2.0 molar hexane solution, 0.4 mmol). After addition of 0.3 g (1.2 mmol) sulfur and stirring at room temperature for 3 h. the mixture was filtered through a short plug of Al$_2$O$_3$ and worked-up in the usual manner, yielding 80 mg (0.2 mmol, 53%) **6**.

Yellow crystals, m.p. 115°C, dec. Anal. Found: C, 58.88; H, 5.60. C$_{16}$H$_{18}$FeN$_2$S. Calcd.: C, 58.91; H, 5.56%. IR(KBr): cm^{-1} 3073w, 2936w, 1692s, 1672s, 1491m, 1439m, 1406s, 1387m, 1350s, 1337m, 1317w, 1169s, 1105w, 1020s, 823s, 806s, 742s, 503s, 484s. MS(EI, 70 eV): m/z(%) 362(46) (M$^+$), 348(63) (M$^+$–CH$_3$), 330(11) (M$^+$–S), 297(35) (M$^+$–Cp), 282(8) (M$^+$–CH$_3$–Cp), 265(23) (M$^+$–Cp–S), 199(100) (FcCH$_2$). ^{1}H NMR (DMSO-d$_6$): d 3.75 (s, 3H, CH$_3$), 4.10 (m, 2H, Cp$_{\mathrm{subst}}$), 4.22 (s, 5H, Cp$_{\mathrm{unsubst}}$), 4.47 (m, 2H, Cp$_{\mathrm{subst}}$), 5.31 (s, 2H, CH$_2$), 7.00–7.22 (m, 4H, benzimidazole). ^{13}C NMR (DMSO-d$_6$): d 31.2 (CH$_3$), 44.2 (CH$_2$), 68.5 (Cp$_{\mathrm{subst}}$), 68.8 (Cp$_{\mathrm{unsubst}}$), 69.7 (Cp$_{\mathrm{subst}}$), 82.1 (C(1) of Cp$_{\mathrm{subst}}$); 108.8, 109.3, 121.1, 122.7 (benzimidazole); 198.0 (C=S). CV (CH$_3$CN; 20°C) [V]: 0.47. X-ray structure (Tables 1 and 4; Fig. 3): single crystals were obtained from dichloromethane/hexane.

4.8. [1,3-Di(ferrocenylmethyl))benzimidazoline-2-ylidene]pentacarbonyl tungsten(0) ***7***, *[1-(ferrocenylmethyl)benzimidazole]pentacarbonyl tungsten(0)* ***8***, *and [1,3-di(ferrocenylethyl))benzimidazoline-2-ylidene] pentacarbonyl tungsten(0)* ***9***

A Schlenk vessel was charged with 0.2 g (0.3 mmol) **3a**-iodide and 70 ml THF. The mixture was cooled to −80°C and lithiated with n-butyl lithium (0.16 ml of a 2.0 molar hexane solution, 0.3 mmol). While this solution was allowed to warm to room temperature, a second Schlenk vessel was charged with 0.5 g (1.4 mmol) W(CO)$_6$ and 30 ml THF, and photolyzed with a 150W high pressure mercury lamp. The resulting solution of W(CO)$_5$ · THF was added to the benzimidazoline-2-ylidene derived from **3a**. After stirring at room temperature for 30 min the mixture was worked-up and chromatographed, yielding 18 mg (0.02 mmol, 6.9%) **7**, 17 mg (0.02 mmol, 8.5%) **8**, and 11 mg (0.02 mmol, 6.2%) 2,3-dihydro-2-butyl-1,3-*bis*(ferrocenylmethyl)benzimidazole. Analogously, metal carbonyl complex **9** was prepared from 0.2 g (0.3 mmol) **5**-iodide by deprotonation with butyl lithium and subsequent reaction with photochemically generated W(CO)$_5$ · THF, affording 57 mg (0.07 mmol, 20.5%) **9**.

Data for **7**: yellow crystals, m.p. 163–165°C. Anal. Found: C, 48.69; H, 3.14. C$_{34}$H$_{26}$Fe$_2$N$_2$O$_5$W. Calcd.: C, 48.72; H, 3.13%. IR(KBr): cm^{-1} 3106w, 2929w, 2060s ($\nu_{C=O}$), 1971s ($\nu_{C=O}$), 1935s ($\nu_{C=O}$), 1479s, 1337s, 1306s, 1161m, 1105s, 1041s, 1028m, 1001s, 825s, 740s, 607s, 592m, 578s, 501s, 486m. MS(FAB): m/z(%) 838(100) (M$^+$), 755(12) (M$^+$–3 CO), 696(34) (M$^+$–5 CO),. ^{1}H NMR (CDCl$_3$): d 4.14 (m, 4H, Cp$_{\mathrm{subst}}$), 4.23 (s, 10H, Cp$_{\mathrm{unsubst}}$), 4.36 (m, 4H, Cp$_{\mathrm{subst}}$), 5.64 (s, 4H, CH$_2$), 7.03–7.36 (m, 4H, benzimidazole). ^{13}C NMR (CDCl$_3$): d 52.0 (CH$_2$), 68.4 (Cp$_{\mathrm{subst}}$), 69.2 (Cp$_{\mathrm{unsubst}}$), 70.1 (Cp$_{\mathrm{subst}}$), 81.6 (C(1) of Cp$_{\mathrm{subst}}$); 111.9, 122.7, 134.7 (benzimidazole); 191.6 (C=O), 197.8 (carbene-C), 200.4 (C=O). CV (CH$_3$CN; 20°C) [V]: 0.53. X-ray structure (Tables 1 and 5; Fig. 4): single crystals were obtained from dichloromethane/hexane.

Data for **8**: yellow crystals, m.p. 197°C. Anal. Found: C, 43.10; H, 2.50. C$_{23}$H$_{16}$FeN$_2$O$_5$W. Calcd.: C, 43.16; H, 2.52%. IR(KBr): cm^{-1} 2068s ($\nu_{C=O}$), 1966s ($\nu_{C=O}$), 1917s ($\nu_{C=O}$), 1896s ($\nu_{C=O}$), 1883s ($\nu_{C=O}$), 1516s, 1460s, 1385w, 1263w, 1240w, 1167w, 1040m, 1028m, 1005m, 823m, 744s, 603s, 580s, 505w, 482w. MS(FAB): m/z(%) 640(100) (M$^+$), 613(10) (M$^+$–CO), 584(40) (M$^+$–2 CO), 553(8) (M$^+$–3 CO). ^{1}H NMR (CDCl$_3$): d 4.20 (s, 5H, Cp$_{\mathrm{unsubst}}$), 4.25 (m, 2H, Cp$_{\mathrm{subst}}$), 4.28 (m, 2H, Cp$_{\mathrm{subst}}$), 5.12 (s, 2H, CH$_2$), 7.44–8.06 (m, 5H, benzimidazole). ^{13}C NMR (CDCl$_3$): d 45.8 (CH$_2$), 69.0 (Cp$_{\mathrm{unsubst}}$), 69.4 (Cp$_{\mathrm{subst}}$); 110.6, 120.8, 124.3, 124.5, 147.3 (benzimidazole); 198.3 (C=O).

Data for 2,3-dihydro-2-butyl-1,3-*bis*(ferrocenylmethyl) benzimidazole: yellow crystals, m.p. 147–151°C. Anal. Found: C, 69.23; H, 6.33. C$_{33}$H$_{36}$Fe$_2$N$_2$. Calcd.: C, 69.25; H, 6.34%. IR(KBr): cm^{-1} 3093w, 2921m, 1601w, 1493s, 1387m, 1373w, 1333w, 1302w, 1265m, 1246m, 1105s, 1026m, 999w, 820s, 764m, 723s, 493s. MS(EI, 70 eV): m/z(%) 573(18) (M$^+$), 516(24) (M$^+$–C$_4$H$_9$), 373(20) (M$^+$–FcCH$_3$), 199(100) (FcCH$_2$).^{1}H NMR (CDCl$_3$): d 0.80–1.24 (m, 9H, H$_3$C-CH$_2$-CH$_2$-CH$_2$), 4.08 (m, 4H, Cp$_{\mathrm{subst}}$), 4.10 (br s, 14H, Cp$_{\mathrm{unsubst}}$ and Cp$_{\mathrm{subst}}$), 4.70 (s, 4H, CH$_2$), 6.33–6.53 (m, 4H, benzimidazole). ^{13}C NMR (CDCl$_3$): d 14.2 (CH$_3$), 22.9 (CH$_2$), 24.2 (CH$_2$), 31.3 (CH$_2$), 46.8 (CH$_2$), 67.7 (Cp$_{\mathrm{subst}}$), 68.1 (Cp$_{\mathrm{subst}}$), 68.5 (Cp$_{\mathrm{unsubst}}$), 83.4 (C(1) of Cp$_{\mathrm{subst}}$); 105.4, 118.0, 141.5 (benzimidazole).

Data for **9**: yellow crystals, m.p. 128°C, dec. Anal. Found: C, 49.87; H, 3.46. C$_{36}$H$_{30}$Fe$_2$N$_2$O$_5$W. Calcd.: C, 49.92; H, 3.49%. IR(KBr): cm^{-1} 2963w, 2929w, 2062s ($\nu_{C=O}$), 1977s ($\nu_{C=O}$), 1950s ($\nu_{C=O}$), 1925s ($\nu_{C=O}$), 1261s, 1134m, 1107s, 1030s, 1001s, 802s, 750m, 740m, 603s, 594s, 578m, 499m, 482m. MS(FAB): M$^+$ not observed. ^{1}H NMR (CDCl$_3$): δ 2.95 (m, 4H, CH$_2$), 4.14 (s, 10H, Cp$_{\mathrm{unsubst}}$), 4.16 (m, 4H, Cp$_{\mathrm{subst}}$), 4.22 (m, 4H, Cp$_{\mathrm{subst}}$), 4.65 (m, 4H, CH$_2$), 7.37 (br s, 4H, benzimidazole). ^{13}C NMR (CDCl$_3$): δ 31.6 (CH$_2$), 51.7 (CH$_2$), 68.3 (Cp$_{\mathrm{subst}}$), 68.4 (Cp$_{\mathrm{subst}}$), 68.7 (Cp$_{\mathrm{unsubst}}$), 83.5 (C(1) of Cp$_{\mathrm{subst}}$); 110.9, 123.4, 134.4 (benzimidazole); 196.4 (C=O), 197.7 (carbene-C), 198.9 (C=O), 200.1 (C=O). CV (CH$_3$CN; 20°C) [V]: 0.43.

4.9. Palladium(II) complexes ***10*** *and* ***11***

A mixture of 0.24 g (0.5 mmol) **2a**-iodide [0.3 g (0.47 mmol) **3a**-iodide, respectively] and 59 mg (0.25 mmol) Pd(II) acetate was refluxed in THF for 30 min. Solvent was removed in vacuo and the solid residue was washed with three portions of ether. The crude product was dissolved in dichloromethane and crystallized by addition of hexane, yielding 178 mg (0.17 mmol, 67%) **10** or 63 mg (0.05 mmol, 19.4%) **11**, respectively.

Data for *trans*-*bis*[1-ferrocenylmethyl-3-methyl-benzimidazoline-2-ylidene]-diiodopalladium(II) **10**: yellow crystals, m.p. not observed up to 330°C. Anal. Found: C, 44.67; H, 3.59. $C_{38}H_{36}Fe_2I_2N_4Pd$. Calcd.: C, 44.72; H, 3.56%. IR(KBr): cm^{-1} 3081w, 2929w, 1479s, 1460m, 1443s, 1404m, 1391s, 1177w, 1107m, 1043m, 1024s, 1001s, 818s, 802s, 750s, 501s, 482s. MS(FAB): m/z(%) 1020(100) (M^+). Due to insufficient solubility and/or decomposition in solution no NMR data could be obtained.

Data for *bis*[1,3-di(ferrocenylmethyl)benzimidazoline-2-ylidene]-diiodopalladium(II) **11**: yellow crystals, m.p. not observed up to 330°C. Anal. Found: C, 50.10; H, 3.80. $C_{58}H_{52}Fe_4I_2N_4Pd$. Calcd.: C, 50.16; H, 3.77%. IR(KBr): cm^{-1} 3093w, 2925w, 1616m, 1514w, 1478s, 1443m, 1410s, 1393s, 1366m, 1339m, 1171w, 1150s, 1041m, 1024m, 1001m, 820s, 742s, 499s. MS(FAB): m/z(%) 1388(30) (M^+), 1189(10) (M^+–$FcCH_2$). ^1H NMR ($CDCl_3$): δ 4.16, 4.21, 4.31, 4.73, 4.76 (16H, each signal: m, CH_2), 4.26 (20H, s, $Cp_{unsubst}$), 5.92 (s, 4H, CH_2), 5.98 (s, 4H, CH_2), 6.98–7.45 (m, 8H, benzimidazole). ^{13}C NMR ($CDCl_3$): δ 45.7, 49.6, 50.8 (CH_2); 68.3, 68.4, 69.0, 69.2, 70.7, 70.8 (Cp_{subst} and $Cp_{unsubst}$); 80.9, 82.3 (C(1) of Cp_{subst}); 110.5, 111.2, 111.8, 121.7, 122.2, 122.3, 123.2, 124.1, 134.6, 134.7, 144.2 (benzimidazole); 179.4 (carbene-C). X-ray structure of *trans–anti* isomer (Tables 1 and 6; Fig. 5): single crystals were obtained from dichloromethane.

*4.10. Mercury(II) complexes **12a,b**, **13**, **14a,b**, **15***

Mixtures of azolium halogenides **2a,b**, **3a,b**, **5** (X = I or Br) were refluxed for 40 min in THF with 0.5 mole equivalents of mercury(II) acetate: 0.2 g (0.4 mmol) **2a**-iodide/70 mg (0.2 mmol) $Hg(OAc)_2$; 212 mg (0.5 mmol) **2b**-iodide/83 mg (0.25 mmol) $Hg(OAc)_2$; 0.2 g (0.3 mmol) **3a**-iodide/50 mg (0.15 mmol) $Hg(OAc)_2$; 228 mg (0.4 mmol) **3b**-iodide/60 mg (0.19 mmol) $Hg(OAc)_2$; 92 mg (0.14 mmol) **5**-bromide/24 mg (0.07 mmol) $Hg(OAc)_2$; respectively. During this reflux period a color change yellow-brown-tan took place. For work-up THF was removed on a rotary evaporator, the residues were washed with three portions of ether, and the crude products were dissolved in dichloromethane and crystallized by addition of a small layer of hexane, resulting in: 90 mg (0.08 mmol, 37%) **12a**; 60 mg (0.04 mmol, 20.7%) **13**; 133 mg (0.13 mmol, 56.6%) **12b**; 50 mg (0.03 mmol, 21.6%) **14a**; 72 mg (0.05 mmol, 27%) **14b**; 55 mg (0.04 mmol, 49%) **15**; respectively.

Data for *bis*[1-ferrocenylmethyl-3-methyl-benzimidazoline-2-ylidene]mercury(II) diiodide **12a**: yellow crystals, m.p. 200°C, dec. Anal. Found: C, 40.88; H, 3.28. $C_{38}H_{36}Fe_2HgI_2N_4$. Calcd.: C, 40.94; H, 3.25%. IR(KBr): cm^{-1} 3077w, 1568w, 1481m, 1458s, 1408m, 1393m, 1377w, 1337w, 1105m, 1041w, 1016m, 1001m, 820s, 798s, 787s, 748s, 501s, 482s. MS(ESI): m/z(%) 987(75) (M^+–I), 659(30) (M^+–2I–$FcCH_2$), 331(100) (1-ferrocenylmethyl-3-methyl-benzimidazole). ^1H NMR (DMF-d_7): d 4.25 (6H, s, CH_3), 4.29 (10H, s, $Cp_{unsubst}$), 4.33–4.80 (8H, m, Cp_{subst}), 5.89 (4H, s, CH_2), 7.51–8.0 (8H, m, benzimidazole). ^{13}C NMR (DMF-d_7): d 30.04 (CH_3); 47.37, 48.03 (CH_2); 69.06, 69.43, 69.63, 70.42, 70.83 (Cp_{subst} and $Cp_{unsubst}$); 112.62, 113.09, 113.44, 113.83, 114.11, 114.33, 125.41, 125.85, 127.28, 142.94 (benzimidazole).

Data for *bis*[1-ferrocenylmethyl-3-methyl-benzimidazoline-2-ylidene]diiodo-$\mu\mu'$-diiodo-dimercury(II) **13**: yellow crystals, m.p. 200°C, dec. Anal. Found: C, 29.02; H, 2.35. $C_{38}H_{36}Fe_2Hg_2I_4N_4$. Calcd.: C, 29.09; H, 2.31%. IR(KBr): cm^{-1} 3075w, 2944w, 1481s, 1456s, 1410s, 1395s, 1346m, 1335s, 1261m, 1103m, 1016m, 816m, 798s, 789m, 766w, 754s, 737s, 499s, 482m. MS(ESI): m/z(%) 1446(4) ($M^+ + H$), 988(100) (M^+–HgI_2), 658(20) (M^+–HgI_4–$FcCH_2$). ^1H NMR (DMF-d_7): d 3.49 (6H, s, CH_3); 5.71, 5.75, 5.81, 5.87, 5.95 (22H, m, $Cp_{unsubst}$, Cp_{subst}, CH_2); 7.54–8.07 (8H, m, benzimidazole). ^{13}C NMR (DMF-d_7) (due to decomposition during accumulation of the FID only a few of the expected signals were observed): δ 69.25, 69.58, 69.67, 70.67, 70.81 (Cp_{subst} and $Cp_{unsubst}$); 113.62, 125.76 (benzimidazole). X-ray structure (Tables 1 and 7; Fig. 6): single crystals were obtained from a saturated DMF solution at −25°C.

Data for *bis*[1-ferrocenylmethyl-3-methyl-imidazoline-2-ylidene]mercury(II) diiodide **12b**: yellow crystals, m.p. 200°C, dec. Anal. Found: C, 35.47; H, 3.21. $C_{30}H_{32}Fe_2HgI_2N_4$. Calcd.: C, 35.51; H, 3.18%. IR(KBr): cm^{-1} 3143w, 3093m, 1634m, 1564m, 1464s, 1439m, 1412s, 1215s, 1105s, 1040m, 1026m, 1001s, 818s, 754s, 733s, 505s, 484s. MS(ESI): m/z(%) 889(100) ($M^+ + 1H$–I). ^1H NMR (DMF-d_7): δ 3.45 (6H, s, CH_3), 4.04 (2H, m, Cp_{subst}), 4.12 (2H, m, Cp_{subst}), 4.27 (10H, s, $Cp_{unsubst}$), 4.49 (2H, m, Cp_{subst}), 4.60 (2H, m, Cp_{subst}); 5.60, 5.79 (4H, s, CH_2); 7.61, 7.72, 7.74, 7.85 (4H, imidazole). ^{13}C NMR (DMF-d_7): d 43.81 (CH_3); 55.31, 55.99 (CH_2); 74.50, 74.72, 75.27 (Cp_{subst} and $Cp_{unsubst}$); 127.59, 128.61, 130.06, 130.50 (imidazole).

Data for *bis*[1,3-di(ferrocenylmethyl)benzimidazoline-2-ylidene]mercury(II) diiodide **14a**: yellow crystals, m.p. 180°C, dec. Anal. Found: C, 46.95; H, 3.50. $C_{58}H_{52}Fe_4HgI_2N_4$. Calcd.: C, 46.98; H, 3.53%. IR(KBr): cm^{-1} 3094w, 2938w, 1634m, 1559s, 1476w, 1447s, 1412s, 1395w, 1319w, 1105s, 1041m, 1028m, 1013w, 1001s, 820s, 794s, 756m, 501s, 482s. MS(ESI): m/z(%) 1356(15) (M^+–I), 1287(53) (M^+–$FcCH_2$), 515(100). ^1H NMR (DMF-d_7): d 4.16 (4H, m, Cp_{subst}), 4.23 (4H, m, Cp_{subst}), 4.31 (20H, s, $Cp_{unsubst}$), 4.72 (4H, m, Cp_{subst}), 4.76 (4H, m, Cp_{subst}), 5.84 (8H, s, CH_2), 7.53–8.27 (8H, m, benzimidazole). ^{13}C NMR (DMF-d_7): d 48.49 (CH_2); 69.36, 69.66, 70.69, 82.56 (Cp_{subst} and $Cp_{unsubst}$); 113.9, 114.38, 125.88, 126.37 (benzimidazole).

Data for *bis*[1,3-di(ferrocenylmethyl)imidazoline-2-ylidene]mercury(II) diiodide **14b**: yellow crystals, m.p. 180°C, dec. Anal. Found: C, 43.39; H, 3.52. $C_{50}H_{48}Fe_4HgI_2N_4$. Calcd.: C, 43.43; H, 3.50%. IR(KBr): cm^{-1} 3087w, 1636m, 1559s, 1464w, 1423m, 1410s, 1385w, 1238m, 1209w, 1105s, 1040s, 1026s, 1001m, 820s, 733m, 515s, 499s, 484s. MS(ESI): m/z(%) 1383(40) (M^+), 1254(8) (M^+–I), 1189(23), 1055(41), 465(100). ^1H NMR (DMF-d_7): d 4.14 (4H, m, Cp_{subst}), 4.21 (24H, $Cp_{unsubst}$ and Cp_{subst}), 4.44 (4H, m, Cp_{subst}), 4.53 (4H, m, Cp_{subst}), 5.23 (4H, s, CH_2), 5.31 (4H, s, CH_2), 7.51, 7.61 (4H, imidazole). ^{13}C NMR was not possible due to decomposition during accumulation of the FID.

Data for *bis*[1,3-di(ferrocenylethyl)benzimidazoline-2-ylidene]mercury(II) dibromide **15**: yellow crystals, m.p. 180°C, dec. Anal. Found: C, 51.52; H, 4.21. $C_{62}H_{60}Br_2Fe_4HgN_4$. Calcd.: C, 51.54; H, 4.19%. IR(KBr): cm^{-1} 3091w, 1632m, 1560m, 1479m, 1462s, 1418s, 1346w, 1261w, 1204w, 1175m, 1103s, 1043m, 1024m, 1003m, 820s, 760s, 499s, 482s. MS(ESI): m/z(%) 1365(0.02) (M^+–Br), 543(100). ^1H and ^{13}C NMR analysis was precluded by insufficient solubility.

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