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N-Heterocyclic carbenes with N-ferrocenyl-N'-methyl-substitution: synthesis, reactivity, structure and electrochemistry

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Abstract

Benzimidazolium salts with one N-ferrocenyl substituent and with one N-methyl substituent are prepared by a synthetic sequence involving coupling of the metallocenyl group to a non-cyclic orthophenylene-diamine precursor, ring closure, and oxidation. From these carbene progenitors a range of carbene derivatives are synthesized, including thiourea, azine, and metal complexes with W(0), Pd(II) and Hg(II). Spectroscopic, structural and electrochemical properties in this series of compounds are compared with those of recently published analogous but methylene-spacered benzimidazoline-2-ylidene derivatives, indicating significant electronic communication between the carbene moiety and the N-ferrocenyl substituent. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Carbene; Benzimidazoline-2-ylidene; Ferrocene; Azine; Iron; Tungsten; Palladium; Mercury; X-ray structure; Electrochemistry

1. Introduction

N-Heterocyclic carbenes are of current interest due to their anticipated advantageous properties as easily modified ligands in metal complexes with catalytic applications [1]. 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 are interested in the steric and electronic influences exhibited by ferrocenyl substituents. Sterically, the ferrocenyl moiety represents a quite bulky group with unique spatial requirements due to its cylindrical shape, and electronically, the powerful donor capacity of ferrocene [2] might in principle be of advantage for an additional stabilization of the electron-deficient carbene moiety. We have previously reported the synthesis, structural properties, and coordination chemistry of imidazoline-2-ylidenes with pendant ferrocenyl substituents [3]. In these systems with remote metallocenyl groups the electronic influence of the ferrocenyl donor is almost negligible, as expected, due to the saturated spacer between the pendant ferrocenyl substituent and the central carbene moiety. The subject of this paper is to study analogous systems with non-spacered directly attached ferrocenyl groups which should transfer electron density onto the carbene moiety and further to coordinated metal fragments. Because of synthetic reasons—as outlined below—we first report on benzimidazoline-2-ylidenes with one N-metallocenyl group and one N'-alkyl group; results on symmetric N,N'-diferrocenyl carbenes will be published in due course [4].

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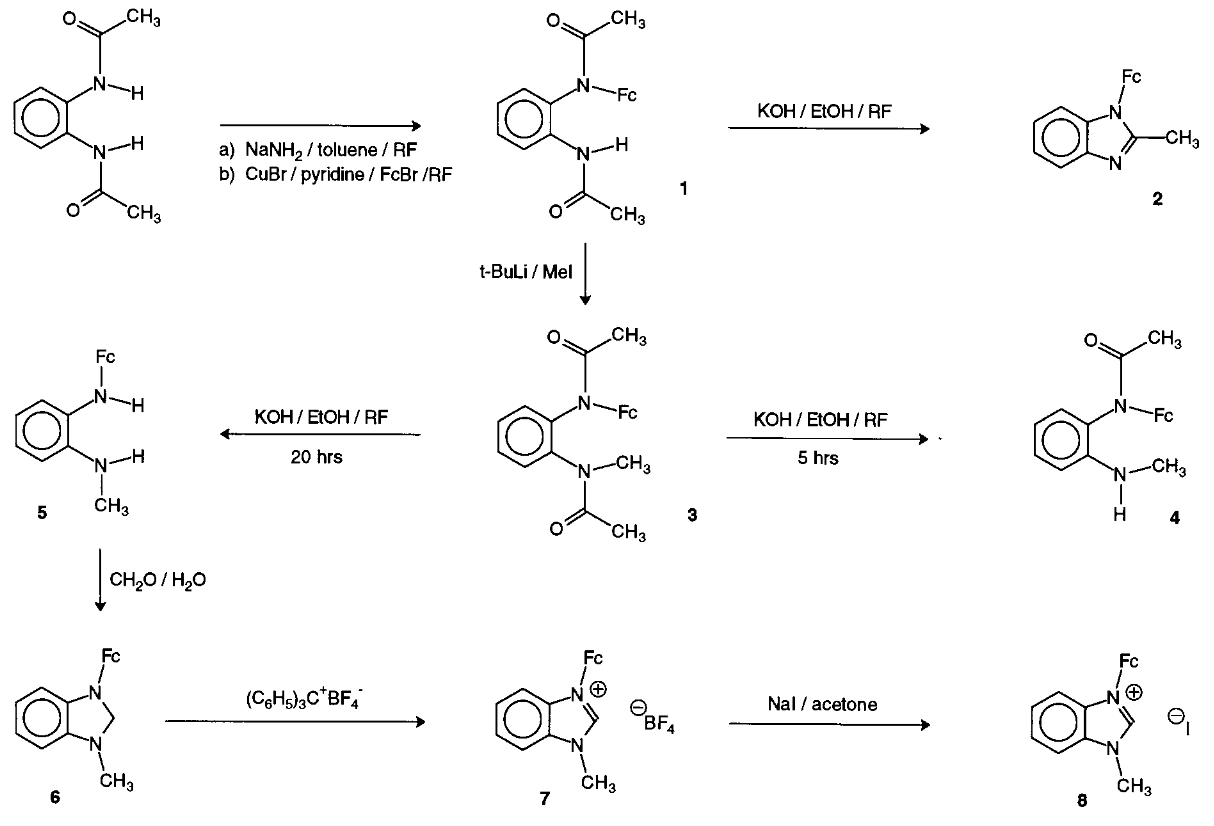


Scheme 1. Synthesis of compounds **1**–**8** (Fc = ferrocenyl).

2. Results and discussion

2.1. Synthesis of N-ferrocenyl azoles

The synthesis of *N*-ferrocenylated azoles is unexpectedly difficult and cannot be achieved by common preparative methods. The only single report on these compounds by Babin and coworkers [5] claimed that ferrocenium salts react with sodium azolides (e.g. imidazolide) in a free radical substitution to afford *N*-ferrocenyl azoles (e.g. *N*-ferrocenylimidazole) which were 'characterized' by observation of the corresponding parent peaks in the mass spectra. However, in our hands this reaction did not work at all under a variety of experimental conditions employing a range of possible staring materials with no indications of trace amounts of the desired ferrocenylimidazole. In addition, other likely methods of synthesis (including Meerwein reactions with *N*-diazonium azoles, substitution reactions starting from *N*-iodo azoles, and others) were investigated by us but met with failure.

Therefore we had to develop a new method of synthesis which relies on (i) linking of the ferrocenyl moiety to a non-cyclic precursor, (ii) subsequent ring closure, and (iii) oxidation to the target azolium salt (Scheme 1).

Step (i) in this synthetic sequence is analogous to the synthesis of ferrocenylamines by cross-coupling reactions of *N*-cuprio-*N*-acetyl ferrocenylamines with bromoferrocene [6,7]. *N*,*N*′-Diacetyl-orthophenylenediamine has been chosen as starting material because its two amino groups are already in a favorable position for the formation of the five-membered ring in step (ii). Interestingly, mono-*N*-substitution with one ferrocenyl group is easily accomplished affording **1** in 62% yield, but all our attempts to effect di-*N*,*N*′-substitution with a second equivalent of ferrocenyl bromide did not afford *N*,*N*′-diferrocenyl-*N*,*N*′-diacetyl-*o*-phenylenediamine, probably due to steric hindrance. This steric hindrance is corroborated by the NMR parameter of **1**, indicating two rotational isomers (compare Section 4). Alkaline hydrolysis of **1** proved possible, but 1-ferrocenyl-2-methylbenzimidazole **2** was obtained—instead of the desired *N*-ferrocenyl-*o*-phenylenediamine—by an intramolecular condensation of mono-deprotected *N*-ferrocenyl-*N*′-acetyl-orthophenylenediamine. Compound **2** is of no further use in *N*-heterocyclic carbene chemistry because its 2-methyl group prevents formation of benzimidazoline-2-ylidene carbenes. We also note that an attempted analogous ferrocenyl substitution reaction with *N*,*N*′-diformyl-orthophenylenediamine as starting material—with acyl groups which cannot take part in such an undesired cyclization—failed.

Whereas attachment of a second (bulky) ferrocenyl group to precursor **1** proved impossible, the corresponding *N*-ferrocenyl-*N*′-methyl derivative **3** could be obtained without problems in 86% yield. Alkaline hydrolysis cleanly afforded mono-deprotected **4** and bis-deprotected *N*-ferrocenyl-*N*′-methyl-orthophenylenediamine **5**, respectively, dependent on duration of the reaction. Condensation with aqueous formaldehyde solution resulted in 1-ferrocenyl-3-methyl-benzimidazoline **6** which was oxidized with trityl tetrafluoroborate as a hydride abstracting reagent [8] in 67% yield to benzimidazolium tetrafluoroborate **7**. Ultrasonic promoted anion exchange with sodium iodide in acetone afforded the corresponding 1-ferrocenyl-3-methyl-benzimidazolium iodide **8**, albeit in a relatively poor yield of 24%.

Both benzimidazolium salts **7** and **8** serve as the key progenitors of all further benzimidazoline-2-ylidene derivatives in this work. Spectroscopically, **7** and **8** show properties which are very similar for both salts and, most important, with a typical ^{1}H- and ^{13}C-NMR signal pattern of 'regular' mono-substituted ferrocenyl groups, indicating no unusual interaction of the directly attached ferrocene donor with the cationic amidinium subunit, thereby ruling out any special metallocene cation stabilization [2] which has been observed in other ferrocenyl substituted cationic compounds. Structurally (Fig. 1, Table 1), the ferrocenyl substituent of **7** is undistorted with bond distances and angles in line with the expectations, but the steric bulk of the ferrocenyl group in comparison to the *N*′-methyl-benzimidazolium part of the molecule is quite evident. As will be seen also in the following structures of carbene-derivatives **11** and **12**, the ferrocenyl substituent is tilted in respect to the plane of the *N*-heterocycle (torsion angle of Cp-plane C(6)–C(7)–C(8)–C(9)–C(10) versus *N*-heterocyclic plane N(1)–C(11)–N(2)–C(13)–C(18) = 37.50(13)°), probably due to crystal packing. The bond lengths and angles of the N(1)–C(11)–N(2) formamidinium subunit (compare Fig. 1) are similar to those of other azolium salts without metallocenyl substituents [1,3].

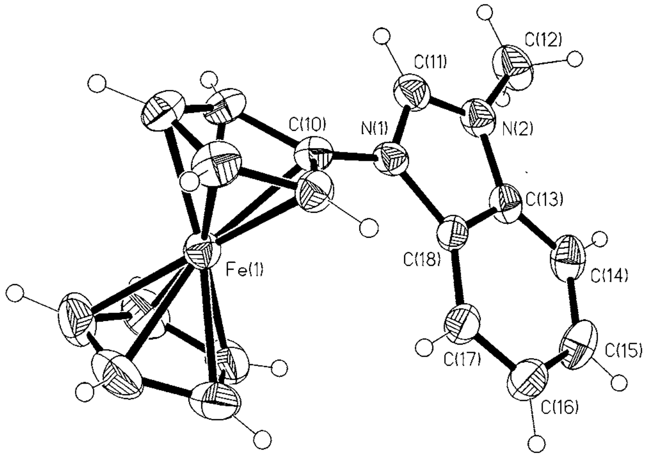


Fig. 1. Molecular structure of the cation of 7, showing the atom numbering scheme. Selected bond distances (pm) and angles (°): N(1)–C(11) = 133.2(5); N(2)–C(11) = 131.2(5); N(1)–C(11)–N(2) = 110.9(3); torsion angle plane C(6)–C(7)–C(8)–C(9)–C(10) vs plane N(1)-C(11)–N(2)–C(13)–C(18) = 37.50(13).

2.2. Carbene derivatives of *N*-ferrocenyl-*N*′-methyl-benzimidazoline-2-ylidene

Azolium salts in general are the most convenient progenitors of *N*-heterocyclic carbenes, formed by abstraction of the proton at the formamidinium carbon by interaction with a suitable base [1]. Such Wanzlick/Arduengo carbenes can either be isolated or prepared in situ and reacted with electrophilic reagents, giving access to a wide range of derivatives. Therefore we were interested in synthesizing a representative number of carbene derivatives of the carbene derived from azolium salts **7** or **8** to study the influence of the *N*-ferrocenyl substituent in comparison to non-metallocenyl systems as briefly outlined in the introduction. Whereas all our attempts to generate and isolate the 'free' carbene *N*-ferrocenyl-*N*′-methyl-benzimidazoline-2-ylidene met with failure—under a variety of experimental conditions with respect to choice of solvent and non-nucleophilic base as summarized in reference [1]—the in situ preparation and derivatization caused no problems. Scheme 2 shows a reaction wheel starting from benzimidazolium salts **7** and **8**.

Deprotonation of **7** with potassium tertiary butoxide in the presence of an excess of elemental sulfur afforded thiourea **9** in 98% yield. Alternatively, thiocarbonylation of orthophenylenediamine **5** with one equivalent of thiophosgene yielded **9** in 49% yield. Interestingly, the ^{13}C chemical shift of the thione carbon (δ (C=S) = 171.09 ppm) of **9** is detected at significantly higher field in comparison to the methylene-spacered analogue 1-(ferrocenylmethyl)-3-methyl-benzimidazoline-2-thione (δ (C=S) = 198.00 ppm [3]), indicating some electron-donation of the *N*-ferrocenyl substituent. This donor-effect is also corroborated by electrochemical measurements (see Section 2.3). Thiourea **9** is a possible starting material for the synthesis of the 'free' carbene *N*-ferrocenyl-*N*′-methyl-benzimidazoline-2-ylidene by reduction with potassium in boiling THF according to the procedure developed by Kuhn [9], however, in our case this method failed and no reaction was observed when **9** and stoichiometric amounts of potassium were refluxed in THF for 2 days. The reason for this unobserved reduction of **9** with alkali metal is probably electronic in origin, because no steric hindrance can be envisaged in this reaction.

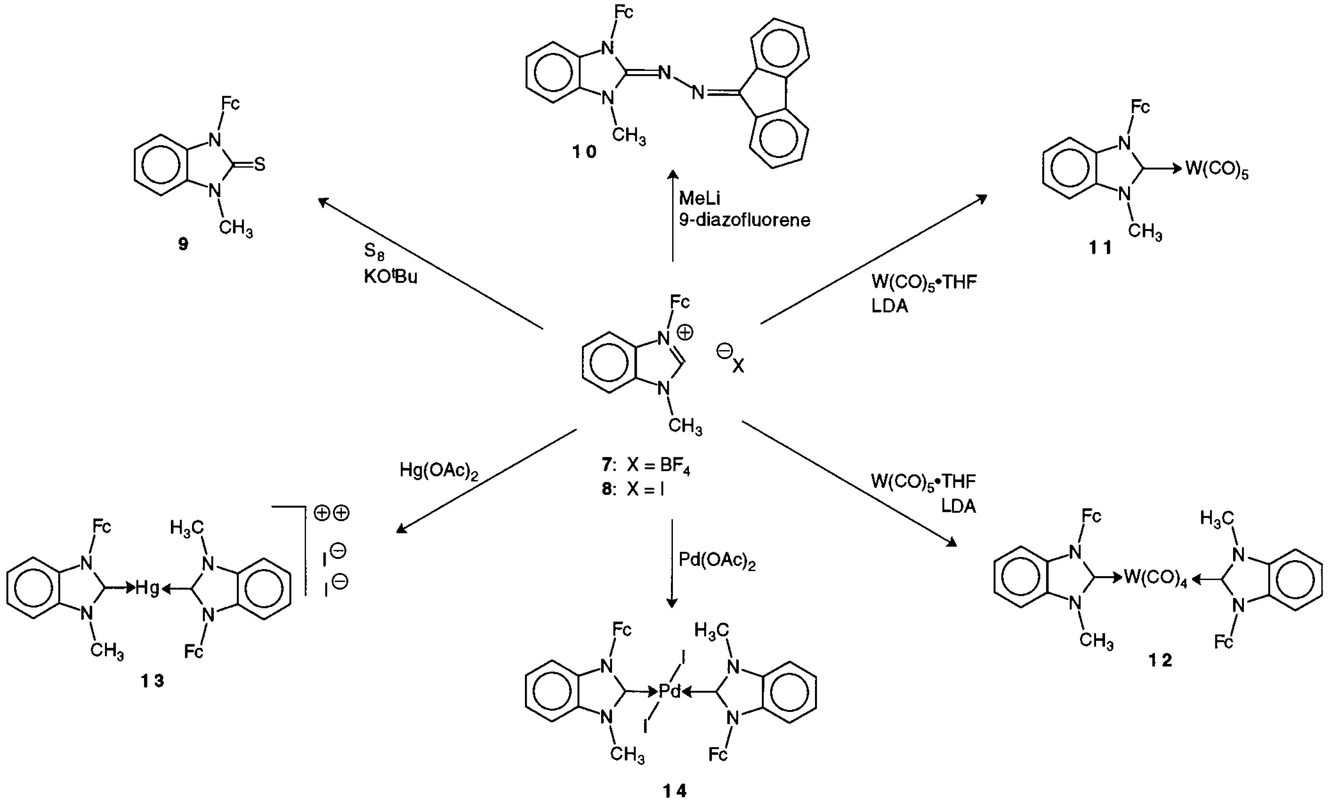
Deprotonation of **7** with methyl lithium and reaction with 9-diazofluorene gives yellow azine **10**, in analogy to such reactivity of Wanzlick carbenes [10,11]. Whereas azine **10** is readily obtained (albeit in a low

Table 1
Crystal data and structure refinement for **7**, **11** and **12**

	7	**11**	**12**
Molecular formula	$C_{18}H_{17}BF_4FeN_2$	$C_{23}H_{16}FeN_2O_5W$	$C_{40}H_{32}Fe_2N_4O_4W \cdot CH_2Cl_2$
Formula weight	404.00	640.08	1013.17
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$ (No.14)	$P2_1/n$ (No.14)	$P2_12_12_1$ (No.19)
a (pm)	1103.0(1)	1095.0(1)	1362.9(2)
b (pm)	1234.7(1)	1277.6(1)	1602.9(2)
c (pm)	1269.4(3)	1541.2(1)	1824.7(2)
α (°)	90	90	90
β (°)	99.85(1)	98.70(1)	90
γ (°)	90	90	90
Volume (nm^3)	1.7033(5)	2.1313(3)	3.9862(9)
Z	4	4	4
Temperature (K)	218	218	213
$D_{calc.}$ (mg m^{-3})	1.575	1.995	1.688
Absorption coefficient (mm^{-1})	0.930	6.112	3.777
$F(000)$	824	1232	2000
Color, habit	Yellow prism	Orange prism	Yellow rectangular prism
Crystal size (mm)	$0.70 \times 0.30 \times 0.20$	$0.40 \times 0.20 \times 0.20$	$0.37 \times 0.37 \times 0.25$
Theta range for data collection (°)	2.80–20.49	2.67–23.99	2.54–22.49
Index ranges	$0 \leq h \leq 12$, $-1 \leq k \leq 13$, $-13 \leq l \leq 11$	$0 \leq h \leq 12$, $-1 \leq k \leq 14$, $-17 \leq l \leq 17$	$-1 \leq h \leq 14$, $-1 \leq k \leq 17$, $-1 \leq l \leq 19$
Reflections collected	1838	3878	3434
Independent reflections	1704 ($R_{int} = 0.0304$)	3319 ($R_{int} = 0.0373$)	3270 ($R_{int} = 0.0319$)
Reflections with $I > 2\sigma(I)$	1488	2990	2992
Absorption correction	None	Ψ-scan	Ψ-scan
Max/min transmission	–	0.822 and 0.538	1.000 and 0.689
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1634/0/255	3239/0/291	3205/2/474
Goodness-of-fit on F^2	1.047	1.088	1.050
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0320$, $wR_2 = 0.0815$	$R_1 = 0.0286$, $wR_2 = 0.0729$	$R_1 = 0.0397$, $wR_2 = 0.0990$
R indices (all data)	$R_1 = 0.0416$, $wR_2 = 0.1038$	$R_1 = 0.0341$, $wR_2 = 0.0774$	$R_1 = 0.0462$, $wR_2 = 0.1035$
Largest difference peak and hole (e nm^{-3})	364 and −220	1717 and −692	1444 and −1128

yield of 22%), the reaction with the extremely reactive and electrophilic 4,5-dicyano-2-diazo-imidazole [12–14] afforded a red solution, most likely an ylidic benzimidazolium-azo-dicyanoimidazolide compound, which proved in our hands too unstable to be isolated in substance, although the positive and negative charge of this azo-spacered zwitter-ion was expected to be highly stabilized by the two heterocyclic termini.

Metal carbene derivatives of the carbene derived from **7** or **8** can be prepared by established methods [1,3] (Scheme 2). Deprotonation with lithium diisopropylamide (LDA) and subsequent reaction with $W(CO)_5THF$ afforded mono-substituted complex **11** in 17.5% yield and (although an excess of $W(CO)_5THF$ was employed) bis-substituted complex **12** as the main product in a yield of 31%. In general, the C=O stretching frequencies in the IR spectrum are a sensitive probe of the electronic properties of ligands in substituted carbonyl metal complexes. The observed values of 2060, 1966 and 1898 cm^{-1} for complex **11** indicate that *N*-ferrocenyl-*N′*-methyl-benzimidazoline-2-ylidene is a quite poor π-acceptor ligand comparable to other imidazoline-2-ylidenes [1]. This effect can be attributed to electron-donation by the directly attached ferrocenyl substituent in **11**, because the otherwise analogous but methylene-spacered compound [1,3-di(ferrocenylmethyl) - benzimidazoline - 2 - ylidene]pentacarbonyl - tungsten(0) shows C=O stretching vibrations of 2060, 1971 and 1935 cm^{-1} [3], comparable to imidazolidine-2-ylidenes [1]. X-ray quality single crystals could be obtained for complex **11** (Fig. 2, Table 1), proving the connectivity of the molecule and allowing comparisons with solid state structures of related carbene–tungsten complexes. The metal–carbene bond distance W(1)–C(11) is 227.0(5) pm, very close in value to the methylene-spacered analogue ($W-C_{carbene} = 226.4(14)$ pm [3]) and the structural features of the coordinated benzimidazoline (compare Fig. 1) are similar to other non-ferrocenylated carbene ligands [1]. The ferrocenyl group is tilted with respect to the benzimidazoline plane (torsion angle of plane C(6)–C(7)–C(8)–C(9)–C(10) versus plane W(1)–C(11)–N(2)–C(13)–C(18) = 49.47(22)°), similar as in the progenitor **7**.



Scheme 2. Synthesis of compounds **9**–**14** (Fc = ferrocenyl).

For the bis-substituted complex **12**, which is formed as the main product in the interaction of in situ generated carbene with W(CO)$_5$THF, cis and trans isomers are in principle possible. Experimentally only the cis isomer is observed according to carbonyl IR stretching vibrations (1991, 1873, 1854 and 1837 cm^{-1}) and as can be seen in the crystal structure of **12** (Fig. 3, Table 1). The two ferrocenyl carbene ligands of **12** show structural parameters analogous to those of mono-substituted complex **11** (**12**: W(1)–C(11) = 226.5(13) pm; W(1)–C(31) = 227.6(13) pm; tilt angles 49.97(61) and 45.53(60)° for ferrocenes Fe(1) and Fe(2), respectively), as anticipated. In addition, for both tungsten complexes **11** and **12** staggered conformations with regard to the benzimidazoline/pentacarbonyltungsten stereochemistry is observed in the crystalline state, obviously a result of intramolecular steric hindrance by the bulky ferrocenyl groups; similar structural features have been reported for other non-metallocenyl carbene pentacarbonyltungsten complexes [1,15].

Reaction of benzimidazolium salt **8** with metal acetates (M(OAc)$_2$; M = Pd^{2+}, Hg^{2+}) yields the expected metal carbene products **13** and **14** by in situ deprotonation with acetate as base and subsequent complex formation. In the case of palladium complex **14**, iodine is necessary as a co-ligand; therefore it is most convenient to start from the corresponding azolium iodide as the carbene progenitor [1,3]. Due to a very poor solubility of both compounds **13** and **14** only IR and mass, but no NMR spectroscopic data are available and, unfortunately, no suitable single crystals could be obtained (in contrast to methylene-spacered analogues [3]). Therefore the true structure of palladium complex **14** with regard to possible different diastereoisomers (cis-trans, trans-syn, trans-anti) cannot be assigned with the limited data available and no comparisons with other *N*-heterocyclic carbene Pd complexes are possible at this point.

2.3. Electrochemistry

One objective of this work has been to evaluate the influence of the directly attached ferrocenyl substituent in these carbene derivatives in comparison to other systems with spacered [3] or without [1] metallocenyl groups. Most conveniently this can be addressed with cyclic voltammetry by comparing relative shifts in the half wave potentials of the ferrocene/ferrocenium (Fc/Fc$^+$) couple. There are, however, some restrictions: because the presence of iodine ligands or counter-ions results in overlapping signals (with respect to the Fc/Fc$^+$ signal) [3], cyclic voltammetry of benzimidazolium salt **7** (but not **8**) was performed and, for similar reasons and more important because of the poor solubility of metal complexes **13** and **14** no data are available for these systems. Table 2 summarizes the electrochemical results obtained for compounds **7**, **9**, **10**, **11** and **12**. As can be seen from inspection of Table 2, the half-wave potentials differ significantly, indicating substantial electronic communication between the ferrocenyl moiety and the carbene subunit.

In comparison to structurally analogous methylene-spacered compounds [3], the observed values of the Fc/Fc$^+$ couple are shifted to higher potentials (**7**: $E_{1/2} = +0.74$ V; CH_2-spacered analogue [3]: $E_{1/2} = +0.57$ V; **9**: $E_{1/2} = +0.51$ V; CH_2-spacered analogue [3]: $E_{1/2} = +0.47$ V) in consonance with increased electron-donation by the directly attached ferrocenyl substituent to the formamidinium or thiourea acceptor moiety.

In the case of azine **10**, five distinct redox processes are observed (Fig. 4). The more cathodic signals at negative potentials are due to three consecutive reductions of the N_2-fluorene part of the molecule in good agreement with results obtained on fluorenone azine ($E_{1/2} = -1.37$, -0.96 V [16]) and benzophenone azine ($E_{1/2} = -1.40$, -0.98 V [17]). The Fc/Fc$^+$ couple correlates most likely to the signal at +0.48 V, close in value to ferrocene itself (FcH/FcH$^+$: $E_{1/2} = +0.42$ V vs saturated calomel electrode (SCE) [18]), and the irreversible signal at +1.04 V can be assigned to an *N*-centered oxidation of the ferrocenyl-*N*-heterocycle, observed at lower potential in comparison to such irreversible *N*-oxidations in non-aromatic ferrocenyl amines ($FcNH_2$: +1.35; Fc_2NH: +1.69; Fc_3N: +1.82 V vs SCE [19,20]).

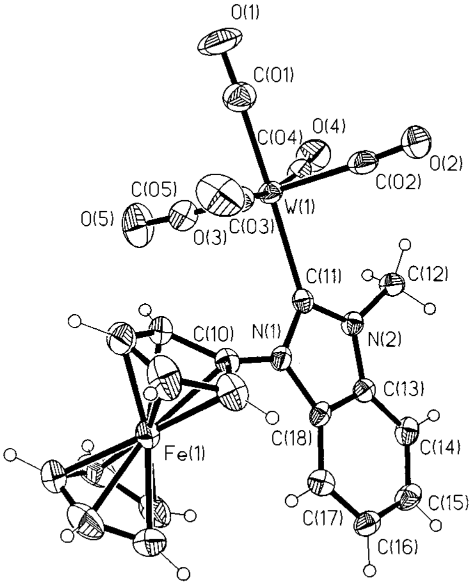


Fig. 2. Molecular structure of **11**, showing the atom numbering scheme. Ferrocene carbons are numbered from C(1) to C(10). Selected bond distances (pm) and angles (°): C(11)–W(1) = 227.0(5); C(11)–N(1) = 138.4(7); C(11)–N(2) = 136.6(6); N(1)–C(18) = 140.9(7); N(2)–C(13) = 138.6(7); C(13)–C(18) = 138.5(7); N(1)–C(11)–N(2) = 104.0(4); C(11)–N(1)–C(18) = 110.8(4); C(11)–N(2)–C(13) = 112.6(4); torsion angle of plane C(6)–C(7)–C(8)–C(9)–C(10) vs plane W(1)–C(11)–N(2)–C(13)–C(18) = 49.47(22).

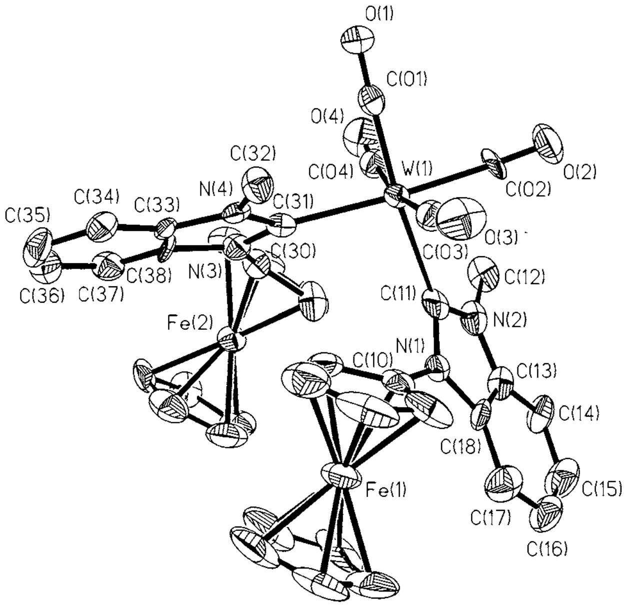


Fig. 3. Molecular structure of **12**, showing the atom numbering scheme. Dichloromethane (solvent molecule) has been omitted for clarity. Ferrocene carbons are numbered for ferrocene Fe(1) from C(1) to C(10), and for ferrocene Fe(2) from C(21) to C(30), respectively. Selected bond distances (pm) and angles (°): C(11)–W(1) = 226.5(13); C(11)–N(1) = 141(2); C(11)–N(2) = 136(2); N(1)–C(18) = 140(2); N(2)–C(13) = 139(2); C(13)–C(18) = 134(2); N(1)–C(11)–N(2) = 103.7(11); C(11)–N(1)–C(18) = 108.7(11); C(11)–N(2)–C(13) = 112.6(12); torsion angle of plane C(6)–C(7)–C(8)–C(9)–C(10) vs plane W(1)-C(11)–N(2)–C(13)–C(18) = 49.97(61); C(31)–W(1) = 227.6 (13); C(31)–N(3) = 136(2); C(31)–N(4) = 139(2); N(3)–C(38) = 140(2); N(4)–C(33) = 138.1(14); C(33)–C(38) = 137(2); N(3)–C(31)–N(4) = 103.2(10); C(31)–N(3)–C(38) = 113.1(10); C(31)–N(4)–C(33) = 111.0(9); torsion angle of plane C(26)–C(27)–C(28)–C(29)–C(30) vs plane W(1)–C(31)–N(4)–C(33)-C(38) = 45.53(60).

For the two tungsten complexes **11** and **12**, the number of detected redox processes (Fig. 5) does not parallel—at first sight—the number of ferrocenyl

Table 2
Cyclic voltammetry[a] of compounds **7**, **9**, **10**, **11** and **12**

Compound number	Formula[b]	$E_{1/2}$ (V vs SCE)
7	$[HL]^+BF_4^-$	+0.74
9	SL	+0.51
10	$C_{13}H_8N_2L$	−1.85, −1.42, −1.06, +0.48, +1.04[c]
11	$[W(CO)_5L]$	+0.59, +1.05[c]
12	$[W(CO)_4L_2]$	+0.37[d], +0.75

[a] In CH_3CN solution with 0.1 M $[(n\text{-}Bu)_4N]PF_6$ electrolyte with a scan rate of 100 mV s^{-1} at 20°C.

[b] L = *N*-ferrocenyl-*N*′-methyl-benzimidazoline-2-ylidene.

[c] Peak potential E_{Pox} of irreversible redox process.

[d] Reversible at a scan rate of 20 mV s^{-1}.

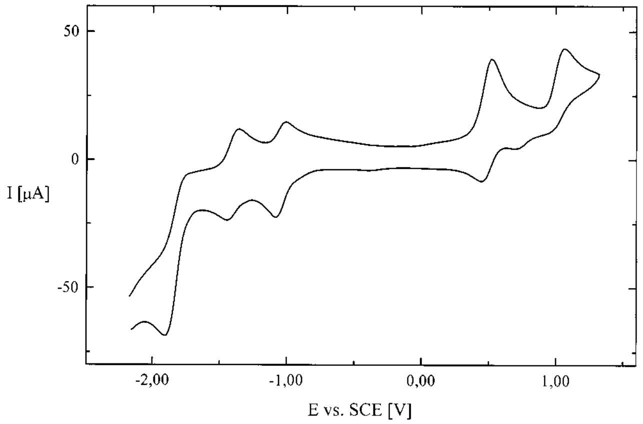


Fig. 4. Cyclic voltammetry of **10**.

groups in these two compounds; in both cases two signals were obtained. Mono-carbene complex **11** exhibits, as expected, a reversible first oxidation at $+0.59$ V which is assigned to the Fc/Fc$^+$ couple and an irreversible second *N*-centered oxidation at a potential similar to that of azine **10**. In contrast, bis-carbene complex **12** shows two reversible waves at $+0.37$ and $+0.75$ V which might be either assigned to two consecutive Fc/Fc$^+$ couples or to one Fc/Fc$^+$ couple followed by a reversible *N*-centered oxidation. Interestingly, the second redox couple in the bis-substituted complex **12** is at a potential similar to that of benzimidazolium tetrafluoroborate **7** (but much lower than all other measured *N*-centered oxidations) indicating quite efficient electronic coupling between the two ferrocenyl groups under the assumption that two consecutive ferrocene oxidations and no *N*-centered oxidation occur in this complex. The pentacarbonyltungsten fragment seems to be a superior acceptor to sulfur (compare $E_{1/2}$ of **9** and **11**) in contrast to a tetracarbonyltungsten(monocarbene) moiety which shifts the first Fc/Fc$^+$ redox process to a potential more negative than those in **9** or in ferrocene, respectively.

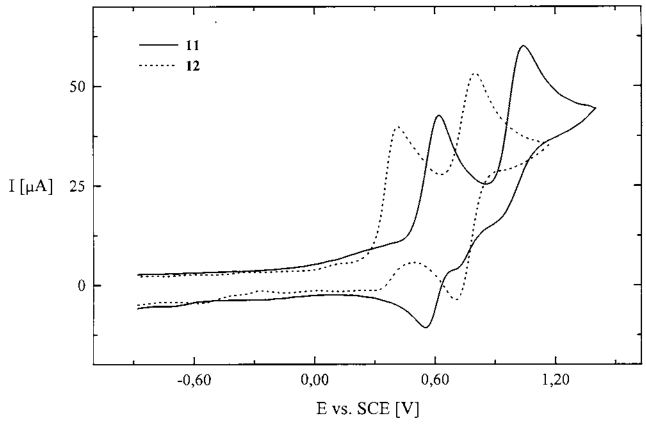


Fig. 5. Cyclic voltammetry of **11** and **12**.

3. Summary and conclusions

The preparation of *N*-ferrocenylated benzimidazolium salts has been achieved by a synthetic sequence of cross-coupling of bromoferrocene with *N*-cuprio-*N*,*N*′-diacetyl-phenylenediamine, *N*′-alkylation, hydrolysis of the acetyl groups, ring closure with formaldehyde, and oxidation with trityl tetrafluoroborate. These are the first azolium compounds with directly attached *N*-ferrocenyl substituents. In situ deprotonation afforded 1-ferrocenyl-3-methyl-benzimidazoline-2-ylidene carbene which was reacted with various selected reagents, yielding the respective thiourea, fluorene azine, and metal complexes of W(0), Hg(II) and Pd(II). Spectroscopic, structural and electrochemical parameters of these *N*-ferrocenyl-*N*-heterocyclic carbene derivatives have been compared with those of non-ferrocenylated and alkyl-spacered analogues, respectively, showing that directly linked ferrocenyl substituents exhibit mainly an electronic inductive donor effect, indicated by the cyclic voltammetry results.

4. Experimental part

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. Standard instrumentation was as recently published [3]. 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 s^{-1}, and 0.1 M tetrabutylammonium hexafluorophosphate ([TBA]PF$_6$) as the conducting salt. The signals were referenced to the SCE by calculating the corresponding half wave potentials from cobaltocenium/cobaltocene as an internal standard versus SCE (cobaltocene: $E_{1/2} = -0.93$ V vs SCE).

4.2. X-ray structure determinations of **7**, **11** and **12**

X-ray crystallographic data (Table 1) were collected by a Siemens P4 diffractometer with graphite-monochromatized Mo–K$_\alpha$ radiation ($\lambda = 71.073$ pm). The unit cell parameters were determined from 25 randomly selected reflections, obtained by P4 automatic routines. Data were measured via ω-scan and corrected for Lorentz and polarisation effects, an empirical absorption correction, based on Ψ-scans, was applied. The structures were solved by direct methods (SHELXS-86) [21] and refined by a full matrix least-squares procedure using F^2 (SHELXL-93) [22]. The function minimized was $\Sigma[w(F_0^2-F_c^2)^2]$ with the weight defined as $w^{-1}=[\sigma^2(F_0^2)+(xP)^2+yP]$ and $P=(F_0^2+2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located by difference Fourier methods, but in the refinement they were included in calculated positions and refined with isotropic displacement parameters 1.2 and 1.5 (for methyl hydrogen atoms) times higher than U_{eq} of the attached atoms. Further details of the crystal structure investigations of **7**, **11** and **12** are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, on quoting the full journal citation.

4.3. N-ferrocenyl-N,N′-diacetyl-o-phenylenediamine **1**

A mixture of 2.18 g (11.3 mmol) *N,N′*-diacetyl-*o*-phenylenediamine and 0.49 g (12.5 mmol) sodium amide in 100 ml toluene was refluxed for 1 h. Solvent and volatile materials were removed in vacuo, the resulting crude white residue was dissolved in 100 ml toluene, and 1.63 g (11.3 mmol) Cu(I)Br, 4 ml pyridine, and 3 g (11.3 mmol) bromoferrocene were added. After refluxing the mixture for 3 days a tan suspension was obtained. Work-up: solvents were removed in vacuo in a rotary evaporator and the crude product was chromatographed on Al_2O_3, first eluting unreacted bromoferrocene and biferrocene with dichloromethane as eluent, and second eluting the product with ethyl acetate as eluent, yielding 2.65 g (7 mmol, 62.1%) **1**. Yellow crystals, m.p. 210°C. Anal. Found: C, 63.59; H, 5.63 $C_{20}H_{21}FeN_2O_2$. Calc.: C, 63.68; H, 5.61%. IR(KBr): cm^{-1} 3314 w (N–H), 2965 w, 1696 s (CO), 1655 s (CO), 1593 s, 1524 s, 1452 s, 1375 m, 1331 s, 1298 m, 1246 w, 1103 m, 1043 w, 829 m, 820 m, 769 s, 486 m, 478 m. MS(EI, 70 eV): *m*/*z*(%) 376(100) (M^+), 334(52) (M^+ −$COCH_3$), 312(26) (M^+ −Cp), 227(36) (FcNCO), 199(47) (FcN), 121(26) (FeCp). ^{1}H-NMR ($CDCl_3$): δ 1.82 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 3.39 (s, 5H, $Cp_{unsubst}$), 4.06 (br s, 2H, Cp_{subst}), 4.09 (br s, 2H, Cp_{subst}), 4.76 (s, 0.5H, NH), 7.16–7.43 (m, 4H, phenylene), 8.32 (s, 0.5H, NH). ^{13}C-NMR (DMSO-d_6): δ 22.67, 23.46, 24.54 (CH_3); 62.25, 63.32, 64.79, 65.73, 68.70 (Fc); 122.96, 123.89, 125.01, 127.25, 128.65, 129.46, 129.99, 134.27, 135.25 (phenylene); 168.68, 169.34 (CO).

4.4. 1-Ferrocenyl-2-methylbenzimidazole **2**

A mixture of 0.145 g (0.4 mmol) **1** and 0.60 g (11 mmol) KOH in Ar-saturated ethanol was refluxed for 3 h. Aqueous work-up yielded 109 mg (0.3 mmol, 89%) **2**. Yellow crystals, m.p. 165–168°C. Anal. Found: C, 68.32; H, 5.12 $C_{18}H_{16}FeN_2$. Calc.: C, 68.38; H, 5.10%. IR(KBr): cm^{-1} 2963 w, 2927 w, 1524 m, 1497 s, 1387 w, 1285 w, 1261 w, 1103 m, 1070 m, 1059 m, 1028 s, 1001 s, 825 s, 800 s, 750 s, 503 s, 486 s, 441 m. MS(EI, 70 eV): *m*/*z*(%) 316(100) (M^+), 251(43) (M^+ −Cp), 195(25) (M^+ −FeCp), 121(39) (FeCp). ^{1}H-NMR ($CDCl_3$): δ 2.61 (s, 3H, CH_3), 4.24 (s, 5H, $Cp_{unsubst}$), 4.26 (m, 2H, Cp_{subst}), 4.56 (m, 2H, Cp_{subst}), 7.16–7.30 (m, 2H, phenylene), 7.62–7.67 (m, 1H, phenylene), 7.97–8.01 (m, 1H, phenylene). ^{13}C-NMR ($CDCl_3$): δ 15.76 (CH_3); 63.40, 65.62, 69.59, 93.72 (Fc); 111.90, 119.01, 122.01, 122.14, 135.52, 142.67, 152.60 (phenylene).

4.5. N-Ferrocenyl-N′-methyl-N,N′-diacetyl-o-phenylenediamine **3**

A solution of 1.673 g (4.4 mmol) **1** in 100 ml THF was cooled to −80°C and metalated with 3.0 ml (4.5 mmol) of a 1.5 molar *t*-butyl lithium solution in pentane. The mixture was allowed to warm to room temperature and 0.28 ml (4.5 mmol) methyl iodide was added. Aqueous work-up yielded 1.5 g (3.8 mmol, 86%) **3**. Yellow crystals, m.p. 193°C. Anal. Found: C, 64.50; H, 5.67 $C_{21}H_{22}FeN_2O_2$. Calc.: C, 64.63; H, 5.68%. IR(KBr): cm^{-1} 2932 w, 1647 s (CO), 1595 s, 1497 s, 1460 s, 1379 s, 1331 m, 1261 w, 1207 w, 1150 m, 1107 w, 1086 w, 1032 w, 1003 m, 937 w, 823 m, 771 m, 727 w, 648 w, 613 w, 571 w, 499 w. MS(EI, 75 eV): *m*/*z*(%) 390(11) (M^+), 332(100) (M^+ −$COCH_3$–CH_3), 325(6) (M^+ −Cp), 267(90) (M^+ −CH_3CO–CH_3–Cp), 121(14) (FeCp). ^{1}H-NMR ($CDCl_3$): δ 1.89 (s, 3H, CH_3), 3.01 (s, 3H, CH_3), 3.12 (s, 3H, CH_3), 3.79 (m, 1H, Cp_{subst}), 3.84 (m, 1H, Cp_{subst}), 3.91 (m, 2H, Cp_{subst}), 4.21 (s, 5H, $Cp_{unsubst}$), 7.08–7.38 (m, 4H, phenylene). ^{13}C-NMR ($CDCl_3$): δ 21.86, 36.26, 40.45 (CH_3); 57.64, 57.84, 63.58, 63.71, 68.06 (Fc); 124.58, 125.72, 128.36, 128.84 (phenylene), 159.63 (CO).

4.6. N-Ferrocenyl-N′-methyl-N′-acetyl-o-phenylenediamine **4**

A mixture of 0.25 g (0.6 mmol) **3** and 2.0 g (36 mmol) KOH in 15 ml Ar-saturated ethanol was refluxed for 5 h. Aqueous work-up yielded 0.199 g (0.5 mmol, 98%) **4**. Yellow crystals, m.p. 100° dec. Anal. Found: C, 65.42; H, 5.77 $C_{19}H_{20}FeN_2O$. Calc.: C, 65.53; H, 5.79%. IR(KBr): cm^{-1} 3299 w (NH), 2961 w, 2927 w, 1655 s (CO), 1605 s, 1589 s, 1530 s, 1483 w, 1470 m, 1458 m, 1385 w, 1314 m, 1142 w, 1105 w, 1070 m, 1047 m, 1036 m, 1020 m, 812 s, 503 w. MS(EI, 75 eV): *m*/*z*(%) 348(100) (M^+), 305(21) (M^+ −$COCH_3$), 283(20) (M^+ −Cp), 239(35) (M^+ −CH_3CO–Cp), 149(85) (M^+ −Fc–CH_3), 121(53) (FeCp). ^{1}H-NMR ($CDCl_3$): δ 1.88 (s, 3H, CH_3), 3.21 (s, 3H, CH_3), 4.06 (m, 2H, Cp_{subst}), 4.16 (s, 5H, $Cp_{unsubst}$), 4.21 (m, 1H, Cp_{subst}), 4.29 (m, 1H, Cp_{subst}), 5.08 (s, 1H, NH), 7.15–

7.23 (m, 4H, phenylene). ^{13}C-NMR ($CDCl_3$): δ 21.94, 35.41 (CH_3); 62.26, 63.07, 64.74, 64.81, 69.02, 98.54 (Fc); 114.14, 118.50, 127.81, 129.12 (phenylene), 172.18 (CO).

4.7. *N-ferrocenyl-N′-methyl-o-phenylenediamine* **5**

A mixture of 0.25 g (0.6 mmol) **3** and 2.0 g (36 mmol) KOH in 30 ml Ar-saturated ethanol was refluxed for 20 h. Aqueous work-up yielded 0.167 g (0.55 mmol, 85%) **5**. Yellow crystals, m.p. dec. Anal. Found: C, 66.73; H, 5.95 $C_{17}H_{18}FeN_2$. Calc.: C, 66.69; H, 5.93%. IR(KBr): cm^{-1} 3357 w (NH), 2963 w, 1603 s, 1516 s, 1495 s, 1452 w, 1435 w, 1283 m, 1263 s, 1165 w, 1105 s, 1040 m, 1022 m, 1001 w, 814 s, 742 s, 488 m. MS(EI, 70 eV): *m*/*z*(%) 306(100) (M^+), 290(37) (M^+ $-CH_3$), 236(45) (M^+ −Cp), 121(54) (FeCp). ^{1}H-NMR ($CDCl_3$): δ 2.85 (s, 3H, CH_3), 3.64 (s, 1H, NH), 3.99 (m, 2H, Cp_{subst}), 4.07 (m, 2H, Cp_{subst}), 4.19 (s, 5H, $Cp_{unsubst}$), 4.35 (s, 1H, NH), 6.69–7.24 (m, 4H, phenylene). ^{13}C-NMR ($CDCl_3$): δ 30.85 (CH_3); 59.58, 63.84, 68.65, 103.78 (Fc); 110.85, 117.87, 118.31, 122.60, 132.94, 141.09 (phenylene).

4.8. *1-Ferrocenyl-3-methyl-benzimidazoline* **6**

A solution of 0.937 g (3.1 mmol) **5** in 20 ml acetone was mixed with 3.0 g of a 35% aqueous solution of formaldehyde (35 mmol) and with 10 ml H_2O. After stirring the mixture at room temperature for 12 h, 100 ml H_2O was added to precipitate the product, yielding 0.543 g (1.7 mmol, 56%) **6**. Yellow crystals, m.p. dec. Anal. Found: C, 67.80; H, 5.72 $C_{18}H_{18}FeN_2$. Calc.: C, 67.94; H, 5.70%. IR(KBr): cm^{-1} 2923 w, 2861 w, 2797 w, 1601 w, 1518 s, 1474 s, 1452 w, 1310 m, 1296 s, 1271 m, 1130 m, 1103 s, 1090 m, 1049 w, 1032 w, 1014 w, 999 w, 833 m, 818 m, 806 m, 740 s, 731 s, 495 s, 486 s. MS(EI, 75 eV): *m*/*z*(%) 318(100) (M^+), 253(5) (M^+ −Cp), 197(22) (M^+ −FeCp), 186(68) (Fc), 121(18) (FeCp). ^{1}H-NMR ($CDCl_3$): δ 2.81 (s, 3H, CH_3), 4.02 (m, 2H, Cp_{subst}), 4.17 (s, 5H, $Cp_{unsubst}$), 4.22 (m, 2H, Cp_{subst}), 4.78 (s, 2H, CH_2), 6.45–7.61 (m, 4H, phenylene). ^{13}C-NMR ($CDCl_3$): δ 34.28 (CH_3); 57.53, 63.79, 68.09 (Fc); 76.32 (CH_2); 105.79, 107.43, 118.76, 119.27 (phenylene).

4.9. *1-Ferrocenyl-3-methylbenzimidazolium tetrafluoroborate* **7**

A solution of 543 mg (1.7 mmol) **6** in 20 ml dichloromethane was cooled to −80°C and 564 mg (1.7 mmol) tritylium tetrafluoroborate was added. The mixture was stirred for 2 h and the product was precipitated by addition of 40 ml ether. Chromatography (Al_2O_3; CH_2Cl_2/CH_3CN 1/1) yielded 0.469 g (1.1 mmol, 67%) **7**. Yellow crystals, m.p. 65°C. Anal. Found: C, 53.41; H, 4.22 $C_{18}H_{17}BF_4FeN_2$. Calc.: C, 53.51; H, 4.24%. IR(KBr): cm^{-1} 3073 w, 1634 m, 1568 s, 1503 w, 1489 w, 1456 w, 1410 w, 1263 w, 1246 w, 1178 w, 1124 s, 1107 s, 1084 s, 1038 s, 1003 s, 866 w, 835 w, 777 w, 758 m, 534 m, 497 m. MS(FAB): *m*/*z*(%) 317(100) (M^+ of cation). ^{1}H-NMR ($CDCl_3$): δ 4.21 (s, 3H, CH_3), 4.33 (s, 5H, $Cp_{unsubst}$), 4.36 (m, 2H, Cp_{subst}), 4.85 (m, 2H, Cp_{subst}), 7.60–7.86 (m, 4H, phenylene), 9.60 (s, 1H, N=CH–N). ^{13}C-NMR ($CDCl_3$): δ 33.68 (CH_3); 64.15, 67.68, 70.49, 91.04 (Fc); 113.37, 113.86, 127.39, 127.50, 132.00, 132.26 (phenylene); 142.11 (N=CH–N). CV (CH_2Cl_2, 20°C) [V]: +0.74. Single crystals were obtained from layering a CH_2Cl_2 solution with n-hexane (Fig. 1, Table 1).

4.10. *1-Ferrocenyl-3-methylbenzimidazolium iodide* **8**

To a solution of 1.824 g (4.5 mmol) **7** in 50 ml acetone was added an excess of sodium iodide and the mixture was sonicated in an ultrasonic cleaning bath for 10 min. Acetone was removed on a rotary evaporator and the residue was washed with portions of H_2O until TLC showed no remaining traces of **7**. In this manner, 0.477 g (1.1 mmol, 24%) **8** was obtained. Yellow crystals, m.p. 198–200°C. Anal. Found: C, 48.59; H, 3.87 $C_{18}H_{17}FeIN_2$. Calc.: C, 48.68; H, 3.86%. IR(KBr): cm^{-1} 3066 m, 2965 m, 1611 m, 1570 s, 1503 w, 1487 w, 1456 m, 1412 w, 1315 w, 1263 m, 1250 m, 1180 w, 1136 w, 1105 m, 1030 w, 1003 w, 866 m, 821 m, 777 m, 756 s, 609 w, 499 s. MS(FAB): *m*/*z*(%) 317(100) (M^+ of cation). ^{1}H-NMR (DMSO-d_6): δ 3.33 (s, 3H, CH_3), 4.40 (s, 5H, $Cp_{unsubst}$), 4.52 (m, 2H, Cp_{subst}), 5.06 (m, 2H, Cp_{subst}), 7.72–8.16 (m, 4H, phenylene), 10.04 (s, 1H, N=CH–N). ^{13}C-NMR (DMSO-d_6): δ 33.45 (CH_3); 63.59, 67.27, 70.15, 91.16 (Fc); 113.87, 114.17, 126.77, 127.05, 131.00, 132.03 (phenylene); 142.99 (N=CH–N).

4.11. *1-Ferrocenyl-3-methyl-benzimidazoline-2-thione* **9**

Method (a) is thionation of the in situ generated benzimidazoline-2-ylidene. A Schlenk vessel was charged with 0.137 g (0.34 mmol) **7** in 20 ml THF, 0.2 g (1.8 mmol) KO^{t}Bu, and 0.3 g (1.2 mmol) sulfur at room temperature. After stirring for 3 h, the mixture was filtered through a short plug of Al_2O_3 and worked-up in the usual manner, yielding 115 mg (0.33 mmol, 98%) **9**.

Method (b) is thiocarbonylation of *ortho*-phenylenediamine **5**. A Schlenk vessel was charged with 2.33 g (7.6 mmol) **5** in 100 ml toluene, 2.2 ml (30 mmol) triethylamine, and 0.58 ml (7.6 mmol) thiophosgene. The mixture was stirred at ambient temperature for 2 days and worked-up in the usual manner, yielding 1.3 g (0.37 mmol, 49%) **9**.

Data for **9**: yellow crystals, m.p. 65°C. Anal. Found: C, 62.13; H, 4.61 $C_{18}H_{16}FeN_2S$. Calc.: C, 62.08; H, 4.63%. IR(KBr): cm^{-1} 2925 w, 1723 m, 1634 s, 1497 s, 1474 m, 1410 m, 1383 m, 1371 m, 1339 s, 1302 m, 1232 m, 1200 s, 1122 w, 1107 w, 1028 w, 1003 w, 874 w, 821 m, 740 s, 632 w, 559 w, 499 s, 424 w. MS(EI, 70 eV): m/z(%) 348(62) (M^+), 283(100) (M^+ −Cp). ^{1}H-NMR ($CDCl_3$): δ 3.88 (s, 3H, CH_3), 4.29 (s, 5H, $Cp_{unsubst}$), 4.34 (m, 2H, Cp_{subst}), 5.08 (m, 2H, Cp_{subst}), 7.18–8.14 (m, 4H, phenylene). ^{13}C-NMR ($CDCl_3$): δ 31.58 (CH_3); 65.37, 65.58, 69.89, 93.44 (Fc); 108.95, 112.04, 122.64, 123.38, 132.33, 132.88 (phenylene); 171.09 (C=S). CV (CH_2Cl_2, 20°C) [V]: +0.51.

4.12. [1-Ferrocenyl-3-methyl-benzimidazoline-2-ylidene]-[fluorene-9-ylidene]-hydrazine **10**

A solution of 0.14 g (0.3 mmol) **7** in 20 ml THF was metalated with 0.23 ml of a 1.5 molar methyl lithium solution (0.3 mmol) in ether at −80°C, the mixture was allowed to warm to room temperature, a solution of 66 mg (0.3 mmol) 9-diazofluorene in 15 ml THF was added dropwise, and stirring was continued for 30 min. Aqueous work-up and chromatography (Al_2O_3; hexane/ether 4/1) yielded 71 mg (0.1 mmol, 22.2%) **10**. Yellow crystals, m.p. 163°C. Anal. Found: C, 73.15; H, 4.75 $C_{31}H_{24}FeN_4$. Calc.: C, 73.24; H, 4.76%. IR(KBr): cm^{-1} 2959 w, 2923 m, 2851 s, 1728 m, 1597 m, 1526 m, 1495 m, 1474 s, 1449 m, 1429 m, 1393 s, 1377 w, 1352 w, 1321 w, 1261 w, 1155 w, 1099 m, 1074 s, 1020 w, 804 w, 733 s. MS(EI, 70 eV): m/z(%) 508(100) (M^+), 443(98) (M^+ −Cp). ^{1}H-NMR ($CDCl_3$): δ 4.13 (s, 3H, CH_3), 4.23 (s, 5H, $Cp_{unsubst}$), 4.31 (m, 2H, Cp_{subst}), 4.94 (m, 2H, Cp_{subst}), 6.90-8.90 (m, 12H, phenylene + fluorene). ^{13}C-NMR ($CDCl_3$): δ 29.69 (CH_3); 64.99, 65.09, 69.35 (Fc); 107.25, 110.96, 119.38, 119.50, 120.02, 120.12, 120.67, 121.42, 121.92, 122.89, 127.08, 127.47, 127.78, 127.93, 128.02, 128.20, 128.23, 128.62, 129.82, 130.96, 131.38 (phenylene + fluorene + C=N–N=C). CV (CH_2Cl_2, 20°C) [V]: −1.85, −1.42, −1.06, +0.48, +1.04.

4.13. [1-Ferrocenyl-3-methyl-benzimidazoline-2-ylidene] pentacarbonyl tungsten(0) **11** and bis[1-ferrocenyl-3-methyl-benzimidazoline-2-ylidene]tetracarbonyl tungsten(0) **12**

A Schlenk vessel was charged with 0.8 g (2.0 mmol) **7** and 200 ml THF. The mixture was cooled to −80°C and lithiated with lithium diisopropylamide (1.0 ml of a 2.0 molar hexane solution, 2.0 mmol). While this solution was allowed to warm to room temperature, a second Schlenk vessel was charged with 1.3 g (3.7 mmol) $W(CO)_6$ and 50 ml THF, and photolyzed with a 150 W high pressure mercury lamp. The resulting solution of $W(CO)_5 \cdot THF$ was added to the benzimidazoline-2-ylidene derived from **7**. After stirring at room temperature for 30 min the mixture was worked-up and chromatographed, yielding 224 mg (0.35 mmol, 17.5%) **11** and 291 mg (0.31 mmol, 31.0%) **12**.

Data for **11**: yellow crystals, m.p. 210°C. Anal. Found: C, 43.08; H, 2.51. $C_{23}H_{16}FeN_2O_5W$. Calcd.: C, 43.16; H, 2.52%. IR(KBr): cm^{-1} 2060 s ($\nu_{C=O}$), 1966 s ($\nu_{C=O}$), 1898 s ($\nu_{C=O}$), 1638 s, 1491 w, 1470 w, 1431 w, 1369 w, 1342 w, 1180 m, 1107 w, 1086 w, 1057 w, 1024 w, 818 m, 754 m, 748 w, 609 w, 590 w, 580 w, 495 w, 478 w. MS(EI, 70 eV): m/z(%) 640(25) (M^+), 612(23) (M^+ −CO), 556(27) (M^+ −3CO), 528(12) (M^+ −4CO), 500(100) (M^+ −5CO). ^{1}H-NMR (CD_2Cl_2): δ 4.12 (s, 3H, CH_3), 4.29 (s, 5H, $Cp_{unsubst}$), 4.46 (m, 2H, Cp_{subst}), 4.86 (m, 2H, Cp_{subst}), 7.37–8.65 (m, 4H, phenylene). ^{13}C-NMR (CD_2Cl_2): δ 37.95 (CH_3), 66.44, 67.71, 70.24 (Fc); 110.38, 114.29, 122.77, 124.00 (phenylene); 198.50, 201.68 (only two out of three low field signals were detected: CO and/or carbene–C). CV (CH_2Cl_2, 20°C) [V]: +0.59, +1.05. Single crystals were obtained from *N*-hexane/CH_2Cl_2 (Fig. 2, Table 1).

Data for **12**: yellow crystals, m.p. 140°C. Anal. Found: C, 51.70; H, 3.45. $C_{40}H_{32}Fe_2N_4O_4W$. Calc.: C, 51.76; H, 3.47%. IR(KBr): cm^{-1} 1991 s ($\nu_{C=O}$), 1873 s ($\nu_{C=O}$), 1854 s ($\nu_{C=O}$), 1837 s ($\nu_{C=O}$), 1638 w, 1495 m, 1472 m, 1427 w, 1362 w, 1337 m, 1317 w, 1290 m, 1263 m, 1173 w, 1153 m, 1128 w, 1105 w, 1074 w, 1061 w, 1022 w, 1003 w, 827 m, 746 m, 615 w, 497 m. MS(EI, 70 eV): m/z(%) 928(9) (M^+), 900(9) (M^+ −CO), 872(11) (M^+ −2CO), 844(9) (M^+ −3CO), 816(20) (M^+ −4CO), 317(100) (ferrocenylmethylbenzimidazoline–2-ylidene). ^{1}H-NMR (CD_2Cl_2): δ 3.88 (s, 6H, CH_3), 4.01 (m, 4H, Cp_{subst}), 4.13 (s, 10H, $Cp_{unsubst}$), 4.46 (m, 4H, Cp_{subst}), 7.24–8.46 (m, 8H, phenylene). ^{13}C-NMR (CD_2Cl_2): δ 37.06 (CH_3), 64.88, 66.28, 69.59, 97.32 (Fc); 109.69, 113.44, 121.75, 123.09, 128.22, 135.42 (phenylene); 209.99 (only one out of three expected low field signals were detected: carbene–C or C = O). CV (CH_2Cl_2, 20°C) [V]: +0.37, +0.75. Single crystals were obtained from n-hexane/CH_2Cl_2 (Fig. 3, Table 1).

4.14. Bis[1-ferrocenyl-3-methyl-benzimidazoline-2-ylidene]mercury(II) diiodide **13**

A mixture of 121 mg (0.27 mmol) **8** and 87 mg (0.27 mmol) mercury(II) acetate was refluxed in THF for 30 min. During this reflux period a color change yellow–brown–tan took place. THF was removed on a rotary evaporator, the residue was washed with three portions of ether, and the crude product was dissolved in dichloromethane and crystallized by addition of a small layer of hexane, yielding 84 mg (0.08 mmol, 28.4%) **13**.

Yellow crystals, m.p. 180°C. Anal. Found: C, 39.68; H, 2.96. $C_{36}H_{32}Fe_2N_4HgI_2$. Calc.: C, 39.79; H, 2.97%. IR(KBr): cm^{-1} 3081 w, 1549 s, 1497 s, 1478 s, 1449 m, 1402 s, 1385 s, 1339 m, 1258 m, 1136 w, 1107 s, 1030 m, 1005 m, 962 w, 872 w, 829 s, 810 s, 752 s, 659 w, 553 w, 497 s. MS(FAB): m/z(%) 961(15) ($M^+ - I + H$), 831(15) ($M^+ - 2I - H$), 645(100) ($M^+ - HgI$). NMR analysis was precluded by insufficient solubility.

4.15. Bis[1-ferrocenyl-3-methyl-benzimidazoline-2-ylidene]diiodopalladium(II) ***14***

A mixture of 0.2 g (0.45 mmol) **8** and 51 mg (0.23 mmol) Pd(II) acetate was refluxed in 25 ml THF for 30 min. During this reflux period a color change yellow–brown–tan took place. THF was removed on a rotary evaporator, the residue was washed with three portions of ether, and the crude product was dissolved in dichloromethane and crystallized by addition of a small layer of hexane, yielding 185 mg (0.2 mmol, 83%) **14**. Yellow crystals, m.p. not observed up to 350°C. Anal. Found: C, 43.47; H, 3.24. $C_{36}H_{32}Fe_2N_4PdI_2$. Calc.: C, 43.56; H, 3.25%. IR(KBr): cm^{-1} 2963 w, 2927 w, 1634 w, 1501 m, 1474 s, 1439 m, 1410 m, 1389 w, 1341 w, 1302 w, 1261 s, 1242 m, 1209 w, 1105 s, 1026 s, 872 w, 804 s, 744 s, 704 w, 497 m, 443 w. MS(FAB): m/z(%) 991.92(100) (M^+). NMR analysis was precluded by insufficient solubility.

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