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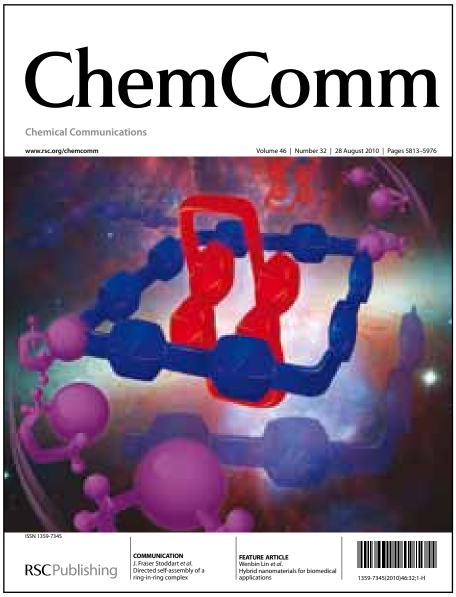

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Carbene spacers in bis-porphyrinic scaffolds

Julien Haumesser, Jean-Paul Gisselbrecht, Jean Weiss* and Romain Ruppert*

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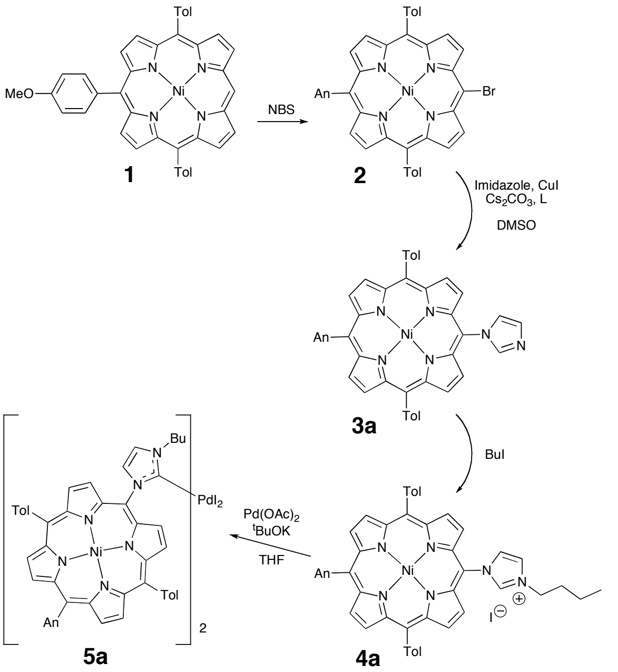
The preparation of two *meso*-imidazolylporphyrins was achieved in good yield by Ullmann coupling between a *meso*-bromotriarylporphyrin and imidazoles. Subsequent alkylation afforded the corresponding imidazolium functionalized porphyrins as direct precursors for the carbene. The complexation of these azolium salts with palladium led to *trans-anti* bis-porphyrin carbenic complexes.

In Nature, imidazole is one of the most encountered ligand for metalloporphyrins. In synthetic inorganic chemistry, the coordinating properties of imidazole have led to the design of several *meso*-2-imidazolyl functionalized porphyrins as precursors of axially linked multiporphyrinic linear or circular arrays.[1,2] In some cases, peralkylation of *meso*-2-imidazolyl porphyrins afforded polycationic water soluble species which were used as catalysts for different oxidation reactions.[3] The recent introduction of two imidazolyl groups through a C-C coupling reaction at two borylated *beta*-pyrrolic positions has opened access to exocyclic chelation of palladium at the periphery of the porphyrin.[4] Imidazolyl groups have also been fused to the pyrrole ring of the porphyrins and been used as precursors of N-heterocyclic carbenes and porphyrinic dimers linked by a palladium ion.[5] This strategy to organize porphyrins around metal ions was used earlier with porphyrins bearing external coordination sites such as pyridines, phosphines, enamino(thio)ketones, or enamino(thio)aldehydes.[6]

Of the C-X coupling reactions possible, the Buchwald-Hartwig aminations are among the most studied for the peripheral functionalizations of porphyrins.[7] However, to the best of our knowledge, the introduction of imidazolyl groups linked to a *meso* position by a nitrogen atom has been much less studied. In an early report, Smith used imidazole as a nucleophile that reacted with the porphyrin radical cation to introduce the imidazolyl group at the *meso* position, but in very poor yields (7%).[8] Aromatic nucleophilic substitution was used more recently to introduce good nitrogen nucleophiles (like alkyl amines or azides) at the brominated *meso* positions of porphyrins.[9]

The *meso* positions of porphyrins are sterically hindered and imidazole is not the best nucleophile. Therefore, we tested if the Ullmann coupling was a feasible method for this C-N coupling.[10] Modern improvements of this old reaction are now available.[11] In our first attempts, 5-iodo-10,15,20-triarylnickelporphyrins was reacted with imidazole in the presence of copper salts and proline[12] to afford the 5-(1-imidazolyl)-10,15,20-triarylnickelporphyrin in 50% yield. Changing the catalytic system for a recently described one (CuI, Cs_2CO_3, phenylbenzoylhydrazine in DMSO at 110 °C)[13] gave even more satisfying yields. Starting from the cheaper and easily accessible brominated derivative **2**, the *meso*-(1-imidazolyl) functionalized porphyrin **3a** could be prepared in 92% yield (see scheme 1).



Scheme 1. Preparation of imidazolium porphyrins (**3a**, **4a**, **5a** for imidazole or **3b**, **4b**, **5b** for benzimidazole functionalized compounds)..

Compound **3a** was characterized by MS (Maldi-TOF: m/z = 719.2) and ^1H NMR (3 additional aromatic signals at 8.37, 7.98, and 7.53 ppm). Alkylation was carried out in neat butyliodide at 110 °C overnight. Again the butylated imidazolium derivative **4a** was easily characterized by MS (Maldi-TOF : m/z = 775.2) and by ^1H NMR (the acidic proton located between the two nitrogen atoms was found at 10.30 ppm). In contrast to most of the imidazolyl functionalized porphyrins, where the carbon between the two nitrogen was not available, in compound **3a** the NHC carbene can now be generated from imidazolium **4a**, like in the fused exemple of

Richeter *and coll.*[5]

Therefore **4a** was reacted with palladium(II) acetate in the presence of a base (^{t}BuOK) at room temperature overnight. Several products were expected: the *cis* and *trans* isomers of a palladium(II) bis(NHC carbene) complex and also the *syn* or *anti* isomers, which were the most probable structures. Experimentally, the starting imidazolium porphyrin was fully consumed and only one major compound was isolated. The MS study showed that this compound was indeed a porphyrin dimer **5a** (MaldiTOF : m/z = 1783.3) that corresponds to the formula of bis(iodo)bis(carbene)Pd(II). At room temperature, the ^{1}H NMR spectrum was quite simple showing that the two porphyrins were equivalent. However, several expected signals were missing. At higher temperature (85 °C in $C_2D_2Cl_4$), these signals could be detected and assigned, indicating that their absence was due to dynamic phenomena, namely rotation of different aromatic groups with the coalescence occuring at room temperature. The two remaining imidazolyl proton signals were observed as two doublets at 7.83 and 6.75 ppm. The butyl proton signals were located around or even below zero ppm (respectively 2.67, 0.07, -0.63, and -0.72 ppm), thus indicating clearly that these groups were exposed to the ring current and sitting on top of a porphyrin ring. According to all spectroscopic data, the *trans-anti* isomer was almost certainly the correct structure. No single crystals suitable for X-ray structure determination could be obtained to confirm these observations.

Therefore, the same reaction sequence was repeated, replacing the imidazolyl group by the benzimidazolyl group. The same chemistry led to similar yields for the benzimidazolyl derivatives **3b** and **4b** and the final isolated dimer **5b** presented very similar spectroscopic characteristics similar to those of **5a**. Single crystals suitable for a structure determination were grown from dichloromethane and ethanol. The bis-carbene palladium complex was indeed the *trans-anti* isomer, which was not surprising from a steric hindrance point of view (see Figure 1). The coordination around the palladium(II) ion was square planar. The Pd-C and Pd-I distances are respectively 2.007 and 2.596 Å. The two nickel porphyrins are ruffled and the nickel(II) coordination is square planar with Ni-N distances around 1.92-1.93 Å. The distance between the two nickel ions is 11.41 Å. The two benzimidazole moieties were almost coplanar and orthogonal to the two porphyrin cores.

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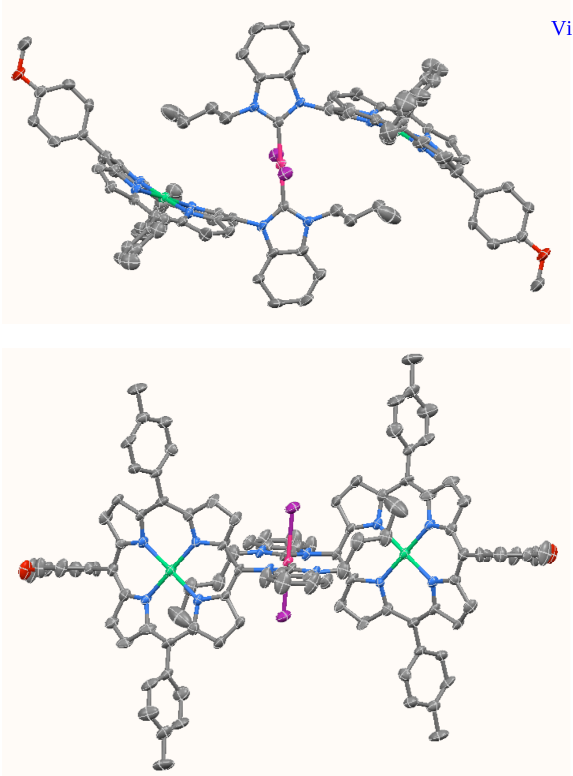

Figure 1. Two orthogonal views of the X-ray structure of **5b**.

The electrochemical data of the two azolyl substituted nickelporphyrins **3a** and **3b** were very similar and typical of nickelporphyrins, with two oxidation and two reduction steps.However, especially for the benzimidazolyl derivative, the first oxidation was spread out over a large potential range, denoting either a slow electron transfer or other electrode surface problems (see SI for cyclic voltammetry curves of monomeric porphyrins). The first reduction step was clearly reversible for both compounds and the other two steps showed less reversible behaviour.

Table 1 Electrochemical data of two monomeric nickelporphyrins **3a** and **3b** and two nickelporphyrin dimmers **5a** and **5b**.[a]

Compound	E_{Red3}	E_{Red2}	E_{Red1}	$E°_{Ox1}$	$E°_{Ox2}$	$E°_{Ox3}$	$E°_{Ox4}$	Ep_{Ox}
NiP **3a**	-2.33	-2.21	-1.64	0.53	0.77			
NiP **3b**	-2.33	-2.18	-1.64	0.59	0.72	0.82		
Dimer **5a**		-2.37	-1.77 (4e$^-$)	0.57	0.65	0.87	0.96	1.15
Dimer **5b**			-1.78 (4e$^-$)	0.58	0.65	0.94	1.00	1.20

[a] Cyclic voltammetry data (V *vs* Fc/Fc$^+$) recorded in dichloromethane with Bu_4NPF_6 (0.1 M) as supporting electrolyte (see SI for experimental details).

The electrochemical study of the two dimers was quite interesting. On the reduction side, a first irreversible step was found at -1.77 V and a second one was close to the electrode discharge. The first reduction is probably the sum of the two porphyrin ring reductions (2 e$^-$) and the linking palladium(II) ion reduction (2 e$^-$).[14] On the oxidation side, four reversible one electron steps were found for the two dimers. This behaviour is quite surprising because splitting of the oxidation waves was observed earlier for conjugated porphyrin dimers.[15] This is not the case here, but the first nickelporphyrin oxidation steps were split by 80 and 70 mV, respectively for **5a** and **5b**. Even the second nickelporphyrin oxidation steps were split with similar separations between the waves. Several years ago, the splitting value of the first oxidation steps was considered as a measure of the electronic communication between two conjugated porphyrins.[15] The values reported here can be compared with the 80 mV splitting reported by Higuchi for an ethylenyl linked NiOEP dimer.[16] Typical splitting values for the first oxidation potentials in porphyrin conjugated dimers are respectively 80 mV, 240 mV, or 400 mV for the ethylenyl and ethynyl linked dimers or for Osuka's triply fused diporphyrins.[15-17]

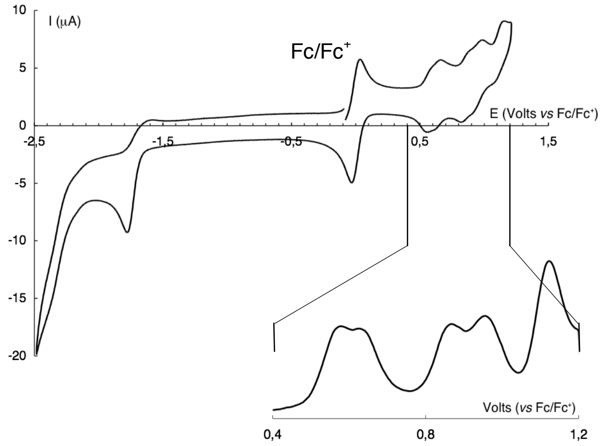

Figure 2. Cyclic voltammetry of **5a** and deconvoluted oxidation curve.

At this stage, intramolecular coulombic effects (between two radical cations and then between two dications) seems the most reasonable explanation for the clear splitting observed here (the shortest distance between the two porphyrins, C-*meso* to C-*meso* is 6.85 Å). However, in porphyrin dimers with similar but even shorter palladium(II) linkages, no splitting was observed.[5] Extremely important splitting values, as high as 240 mV, were observed for cofacial nickelporphyrins, but the intermediate formation of the neutral-radical cation dimer was invoked for this high value.[18] Further studies of similar compounds containing identical or different connections as well as calculations might be needed to fully understand the interactions between the two macrocycles.

In conclusion, the modern Ullmann coupling reaction allowed the introduction of an imidazolyl group at the *meso* positions of porphyrins. These derivatives were used to generate new NHC carbenic species and palladium(II) linked porphyrin dimers. Preliminary tests using the same coupling reaction twice with 5,15-dihalogenated porphyrins led to *meso*-bis(imidazolyl)porphyrins. Work in progress should lead to larger porphyrin scaffolds.

Institut de Chimie, UMR 7177 du CNRS, Université de Strasbourg, 1 rue Blaise Pascal, 67008 Strasbourg cedex, France. Tel: ++(33) 368851700; E-mail: rruppert@unistra.fr, jweiss@unistra.fr.

† Electronic Supplementary Information (ESI) available: [detailed experimental part : preparation and characterization of the new compounds, additional electrochemical data]. CCDC reference number 898396. See DOI: 10.1039/b000000x/

‡ Crystal data for **5b**. From CH_2Cl_2/EtOH, $C_{104}H_{84}N_{12}Ni_2O_2Pd$, M = 2011.45, 0.40×0.28×0.05 red prisms, monoclinic, space group P 21/c, a = 16.311(3) Å, b = 26.899(5) Å, c = 13.696(2) Å, α = 90.00, β = 109.885(4), γ = 90.00, V = 5651.1(17) Å^3, Z = 2, T = 173 K, MoKα = 0.71073, 1.75 < θ < 27.83, 13185 reflections measured, 6059 unique reflections, R_1 = 0.0887, wR_2 = 0.2348, GoF = 0.958.

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