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Facile synthesis of a novel sapphyrin and its rhodium(I) complex

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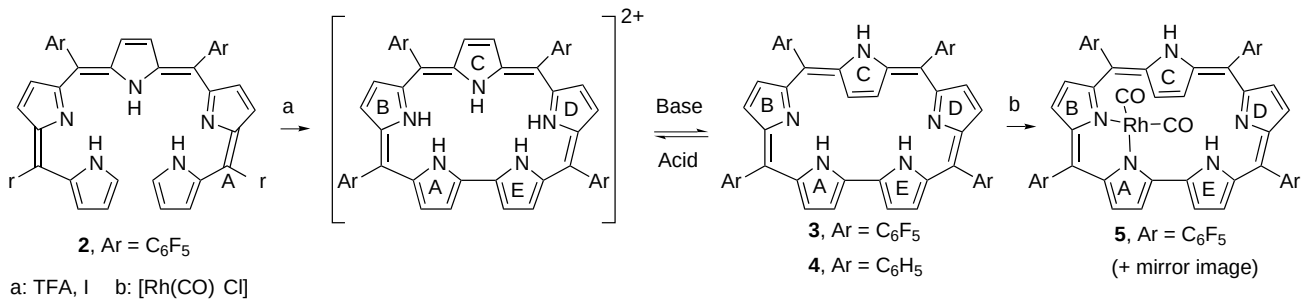
Abstract—The rhodium(I) complex of the novel *meso*-pentafluorophenylsapphyrin is obtained in very high yield by oxidation of the corresponding open-chain pentapyrrole by iodine or oxygen, followed by metallation.

The last few years have witnessed a very large increase in the range of new pyrrole-based macrocycles and linear oligomers, obtained via changes in the reaction conditions that were originally optimized for obtaining porphyrins from pyrrole and aldehydes.[1,2] We have recently contributed to this field by disclosing the solvent-free condensation of pyrrole and electron-poor aldehydes as a novel route to the one-pot synthesis of corroles.[3] With pentafluorobenzaldehyde, two products were isolated (11% yield each) and fully characterized: 5,10,15-tris(pentafluorophenyl)corrole (**1**) and the open-chain pentapyrrole **2** (Scheme 1).[4] Considering the close contact between the terminal pyrroles in the X-ray crystal structure of **2** and bearing in mind the literature regarding oxidative cyclization of open-chain oligopyrroles,[5] it appeared surprising that the corresponding cyclic pentapyrrole (a sapphyrin) was not obtained under the reaction conditions. In addition, **2** appears to be a rational precursor for larger cyclic oligopyrroles. Accordingly, we have examined the reactivity of **2**, obtained in large amounts due to our intensive work with **1** and its metal complexes.[6]

Based on the report by Sessler and co-workers,[5a] the possible transformation of **2** into the corresponding sapphyrin was investigated with $Na_2Cr_2O_7$/TFA. Examination of the crude reaction mixture by NMR spectroscopy revealed the quantitative formation of a product (**3**) with new low-field resonances, consistent with the β-pyrrole protons of an aromatic porphyrin-like macrocycle. In parallel, we checked if the corresponding pentaphyrin can be prepared by reacting **2** with pentafluorobenzaldehyde under catalysis by TFA or $BF_3{\cdot}OEt_2$, followed by DDQ oxidation. Surprisingly, the same product as above (**3**) was obtained (TLC, NMR). Chromatographic workup in order to release **3** from the other components of these reactions (chromate salts, DDQ and its reduced products) resulted in a very low yield of the desired compound. In addition, **3** was contaminated by a yet unidentified decomposition product, which was either absent or present in only minute quantities before chromatography. Accordingly, we looked for alternative oxidants that would allow the preparation of **3** without requiring chromatographic



Scheme 1. Preparation of sapphyrin **3** and its rhodium(I) complex **5**, obtained in >90% yield from **2**.

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treatment (Scheme 1). Two systems were found to fulfill these requirements, iodine and oxygen, in both cases under acidic conditions (in non-acidic solutions, **2** is inert to both I_2 and O_2). Thus, treating a solution of 20 mg **2** in 20 mL benzene and 0.2 mL TFA with 9 mg I_2 for 15 min or by a stream of O_2 for 2 h at room temperature allowed the isolation of **3** in quantitative yield by simply evaporating the solution to dryness.

The identification of **3** as 5,10,15,20-tetra(pentafluorophenyl)sapphyrin is based on MS, ^{1}H and ^{19}F NMR. In common to all other sapphyrins,[7] the diprotonated form of **3** yields a resolved spectrum wherein the resonances of all ten β-pyrrole protons are located at the aromatic region (8.8–10.3 ppm, divided into four doublets and one singlet in accordance with C_{2v} symmetry). For 5,10,15,20-tetraphenylsapphyrin (**4**, previously obtained in 1.1% yield from the condensation of pyrrole and benzaldehyde),[8] Latos-Grazynski and coworkers have shown that the neutral form contains one inverted pyrrole ring (C in Fig. 1) with $CH_{\beta\text{-pyrrole}}$ and NH resonances at unusually low and high field, respectively. Our attempts to obtain the neutral form of **3** revealed that it is very unstable and converts with time into the earlier mentioned decomposition products. This readily explains the instability of **3** to chromatographic treatment. Accordingly, we decided to use non-purified **3** for the next synthetic step.

Insertion of rhodium into **3** appeared to be a very facile process, resulting in the stable rhodium complex **5** (Scheme 1). In fact, the transformation from **2** to **5** in a one-pot/two-step procedure is achieved in an overall yield of more than 90%.[9] The ^{1}H NMR spectrum of **5** (Fig. 1) is highly informative, revealing all the details required for structural elucidation. First note the sharpness of all signals, indicating that the complex is diamagnetic and, accordingly, contains either mono- or trivalent rhodium. The two (out of three in the metal-free sapphyrin **3**) NH resonances support a rhodium(I) oxidation state, wherein the macrocycle acts as a bidentate and monanionic ligand. Secondly, the eight different *ortho*-F, the four different *para*-F, and the ten different mutually coupled $CH_{\beta\text{-pyrrole}}$ resonances ($^3J_{HH}$ = 4.4–5.0 Hz) rule out coordination of the rhodium on the C_2 axis of **3** (utilizing rings A and E). Finally, the $CH_{\beta\text{-pyrrole}}$ resonances at −1.48 and −2.49 ppm and their coupling to the NH signal at 11.79 ppm ($^4J_{HH}$ = 1.4 Hz) indicate that ring C in **5** is inverted. Accordingly, the structure of **5** is similar to that of a fully characterized iridium sapphyrin by means of the coordination of the metal to rings A and B,[10] but dissimilar to it by means of its inverted pyrrole ring C. The more traditional conformation is much less favored for **5**, as may be appreciated by the ten less intense doublets in Fig. 1 (Note: full separation of the two conformers is achievable by preparative TLC). This might explain the failure to introduce a second rhodium ion into **5**, as was achieved for sapphyrins that do not contain an inverted pyrrole ring.[10]

In conclusion, we have demonstrated the facile oxidative cyclization of an open-chain methine-bridged pentapyrrole to sapphyrin, with either iodine or molecular oxygen as oxidants. These mild reaction conditions allowed the isolation of this quite unstable macrocycle in high yield without any chromatographic treatment. In addition, a stable monorhodium complex with an inverted pyrrole is obtained in high yield. Initial results show that **5** is an interesting cyclopropanation catalyst (a product ratio of 3.1(*trans*):1(*cis*) is obtained in the reaction of styrene with ethyl diazoacetate) and future studies will be devoted to the resolution of **5** (note its C_1-symmetry) into its enantiomers for an investigation into their use as asymmetric catalysts.

Acknowledgements

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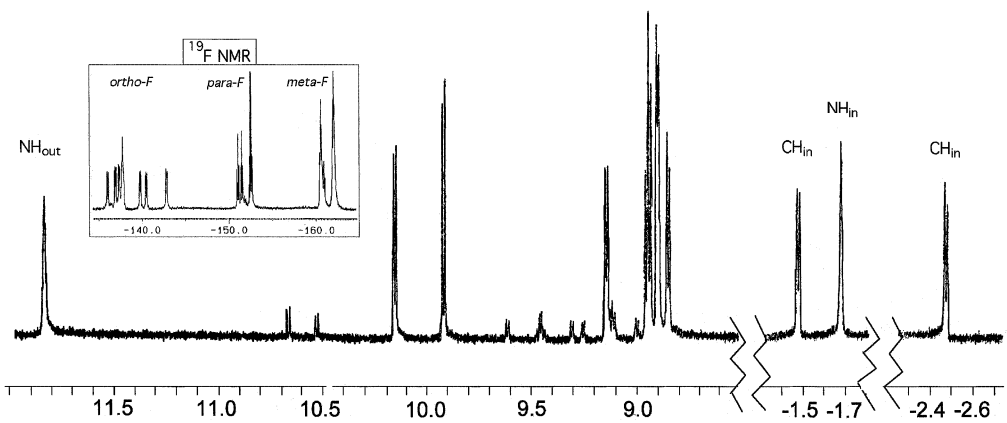

Figure 1. The ^{1}H (400 MHz) and ^{19}F NMR (188 MHz) spectra of the rhodium sapphyrin **5**. The resonances marked as CH_{in} and NH_{out} are the $CH_{\beta\text{-pyrrole}}$ and NH resonances, respectively, of the inverted pyrrole.

References

1. For a recent review, see: Sessler, J. L.; Gebauer, A.; Weghorn, S. J. *The Porphyrin Handbook*; Pergamon: Oxford, 2000; Vol. 2, pp. 55–121.
2. For some recent publications, see: (a) Gryko, T. D. *J. Chem. Soc., Chem. Commun.* **2000**, 2243; (b) Ka, J. W.; Cho, W. S.; Lee, C. H. *Tetrahedron Lett.* **2000**, *41*, 8121; (c) Geier, G. R.; Ciringh, Y.; Li, F. R.; Haynes, D. M.; Lindsey, J. S. *Org. Lett.* **2000**, *2*, 1745; (d) Shin, J. Y.; Furuta, H.; Osuka, A. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 619.
3. Gross, Z.; Galili, N.; Saltsman, I. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1427.
4. Gross, Z.; Galili, N.; Simkhovich, L.; Saltsman, I.; Botoshansky, M.; Bläser, D.; Boese, R.; Goldberg, I. *Org. Lett.* **1999**, *1*, 599.
5. (a) Sessler, J. L.; Seidel, D.; Lynch, V. *J. Am. Chem. Soc.* **1999**, *121*, 11257; (b) Richter, D. T.; Lash, T. D. *Tetrahedron Lett.* **1999**, *40*, 6735.
6. (a) Gross, Z.; Galili, N.; Simkhovich, L. *J. Chem. Soc., Chem. Commun.* **1999**, 599; (b) Gross, Z.; Galili, N. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2366; (c) Simkhovich, L.; Galili, N.; Saltsman, I.; Goldberg, I.; Gross, Z. *Inorg. Chem.* **2000**, *39*, 2704; (d) Simkhovich, L.; Goldberg, I.; Gross, Z. *J. Inorg. Biochem.* **2000**, *80*, 235; (e) Meier-Callahan, A. E.; Gray, H. B.; Gross, Z. *Inorg. Chem.* **2000**, *39*, 3605; (f) Gross, Z.; Golubkov, G.; Simkhovich, L. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 4045; (g) Bendix, J.; Dmochowski, I. J.; Gray, H. B.; Mahammed, A.; Simkhovich, L.; Gross, Z. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 4048; (h) Bendix, J.; Golubkov, G.; Gray, H. B.; Gross, Z. *J. Chem. Soc., Chem. Commun.* **2000**, 1957; (i) Simkhovich, L.; Mahammed, A.; Goldberg, I.; Gross, Z. *Chem. Eur. J.* **2001**, *7*, 1041.
7. Rachlewicz, K.; Latos-Grazynski, L.; Gebauer, A.; Vivian, A.; Sessler, J. L. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2189.
8. Chmielewski, P. J.; Latos-Grazynski, L.; Rachlewicz, K. *Chem. Eur. J.* **1995**, *1*, 68.
9. Synthesis of **5**: 20 mg (19.2 μmol) of **2** was dissolved in 20 mL of benzene and about 0.2 mL of TFA and 8–10 mg of I_2 were added. After stirring the reaction mixture for 15–20 min under air at rt, the solvent was evaporated and the solid material was dried under high vacuum to remove traces of TFA and I_2. The dry solid (**3**) was re-dissolved in a mixture of benzene (30 mL) and triethylamine (1 mL) and the reaction mixture was dried via distillation of 3 mL. This was followed by addition of 35 mg (90 μmol) of $[Rh(CO)_2Cl]_2$ at reflux under argon. The reaction was complete within about 15 min (TLC), after which time the solvents were evaporated under vacuum. Purification of the resulting material from inorganic impurities was performed by flash chromatography on silica gel with *n*-hexane:CH_2Cl_2 (1:2) as eluent. The yield from several syntheses was in the range of 20.5–21.5 mg (90–94% yield). MS (DCI) m/z: 1196.9 ([M^-], 100%). UV–vis (CH_2Cl_2) λ_{max}: 506 nm. ^{19}F NMR ($CDCl_3$, 188 MHz, δ in ppm, J in Hz): −136.10 (dd, $^1J=24.44$, $^2J=8.08$, 1F, *ortho*-F), −136.97 (dd, $^1J=22.94$, $^2J=7.14$, 1F, *ortho*-F), −137.48 (dd, $^1J=23.12$, $^2J=8.46$, 1F, *ortho*-F), −137.83 (dd, $^1J=23.93$, $^2J=4.79$, 1F, *ortho*-F), −139.98 (d, $J=22.18$, 1F, *ortho*-F), −140.48 (d, $J=19.18$, 1F, *ortho*-F), −132.73 (d, $J=22.75$, 1F, *ortho*-F), −150.39 (t, $J=20.87$, 1F, *para*-F), −150.85 (t, $J=20.87$, 1F, *para*-F), −152.49 (m, 2F, *para*-F), −160.18 (m, 4F, *meta*-F), −162.02 (m, 4F, *meta*-F). ^1H NMR ($CDCl_3$, 400 MHz, δ in ppm, J in Hz): 11.79 (s, 1H, NH-inverted), 10.15 (dd, $^1J=4.68$, $^2J=1.32$, 1H, β-pyrrole), 9.92 (d, $J=4.68$, 1H, β-pyrrole), 9.13 (d, $J=4.44$, 1H, β-pyrrole), 8.93 (m, 2H, β-pyrrole), 8.89 (m, 2H, β-pyrrole), 8.84 (dd, $^1J=4.56$, $^2J=1.32$, 1H, β-pyrrole), −1.48 (dd, $^1J=4.90$, $^2J=1.50$, 1H, β-pyrrole inverted), −1.69 (s, 1H, NH), −2.48 (dd, $^1J=4.99$, $^2J=1.47$, 1H, β-pyrrole inverted).
10. Burrell, A. K.; Sessler, J. L.; Cyr, M. J.; McGree, E.; Ibers, J. A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 91.