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Tripyrrin—the missing link in the series of oligopyrrolic ligands

Martin Bröring* and Carsten D. Brandt

Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany.
E-mail: Martin.Broering@mail.uni-wuerzburg.de

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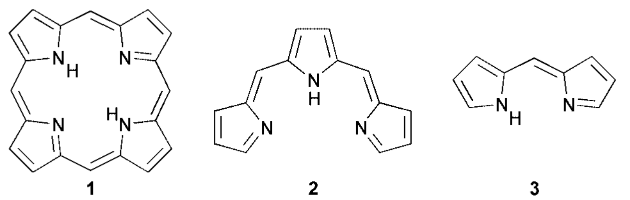
The first derivative of the hitherto elusive tripyrrin 2 was prepared and characterized; the X-ray structural analysis of its trifluoroacetato-palladium(II) complex 7 displays a highly flexible N_3 ligand.

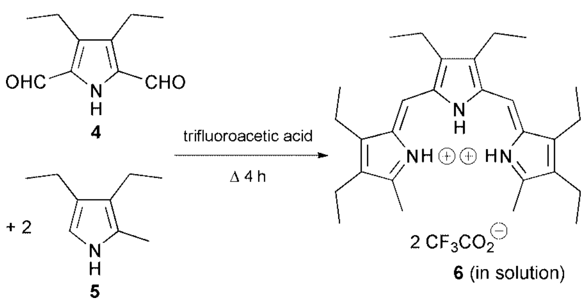
Porphyrin **1**[1] and dipyrrin **3**[2] (Scheme 1) are long-known ligands of related composition, and the co-ordination properties of both as well as the use of the latter in the construction of oligopyrrolic macrocycles[3] has been the topic of numerous investigations over the last century. While **1** and **3** have attracted considerable interest it is remarkable, that the structural link between porphyrins **1** and dipyrrins **3**, the tripyrrin **2**, has remained elusive so far.



Scheme 1

The absence of reports using tripyrrins as ligands is even more surprising, if one takes into account, that the metal complexes of known monoanionic, T-shaped, tridentate N ligands are rather rare studying objects for co-ordination chemists.[4] Only one attempt to produce a tripyrrin **2** has been reported so far. Sessler *et al.* subjected a tripyrrane to oxidizing conditions and observed the unexpected formation of a tripyrrinone-Cu(II) complex, which carries an oxo functionality on one of the *meso* positions.[5] Other tripyrrolic, though dianionic ligands have been described as the free base as well as in metal complexes.[6] As part of our program to explore the co-ordination chemistry of open-chain oligopyrrolic ligands we attempted to close this gap, using the simple synthetic strategy illustrated in Scheme 2.

When the pyrrolic precursors **4** and **5** are condensed *via* the standard conditions for the preparation of dipyrrins (HBr in hot MeOH), the anticipated reaction does in fact occur. The product, however, is not stable in this medium and decays before isolation can be effected. This decay is not observed if boiling trifluoroacetic acid is used as both reagent and solvent. The resulting dark violet–blue solution obtained this way contains mainly **6**[7] and remains remarkably stable for months. All attempts to purify the compound or grow crystals of 3,4,8,9,13,14-hexaethyl-2,15-dimethyltripyrrin **6** have hitherto led to decomposed material only. However, the solvent can be removed *in vacuo* with only little degradation, thus allowing the detection of the organic cation of tripyrrin **6** by means of HRMS.[8] Most probably, **6** is particularly prone to nucleophilic attack at the *meso*-situated CH groups, since one of the electron-poor azafulvene substructures is not balanced by a second electron-rich pyrrole moiety. For further characterization of **6** the condensation of **4** with **5** was carried out in trifluoroacetic acid-d_1, and the resulting solution was analyzed by NMR spectroscopy. The ^{1}H and ^{13}C NMR spectra show mainly the signals of one compound, which are by number and multiplicity in agreement with the proposed structure of tripyrrin **6**. The most prominent absorptions are those for the *meso* CH groups at 7.32 (^{1}H) and 120.8 ppm (^{13}C), respectively. Albeit the spectra indicate a C_{2h} symmetric molecule, the *cisoid* arrangement of the diprotonated tripyrrin **6** could not be concluded from the NMR data. The similarity of the uv/vis absorptions of **6** and the Pd(II) complex **7**, however, supports a conformation as displayed in Scheme 2.



Scheme 2

When all volatiles are evaporated from the dark violet–blue trifluoroacetic acid solution and the residue is treated with a slurry of excess palladium(II) acetate and sodium acetate in MeOH, a green solution is formed immediately. From this, the trifluoroacetatopalladium(II) complex **7** can be isolated by chromatography and subsequent crystallization from dichloromethane/*n*-hexane in 55% yield (calculated from **4**).[9] As the X-ray crystallographic study[10] revealed, **7** is indeed the first co-ordination compound of an intact, monoanionic tripyrrin ligand (Fig. 1).

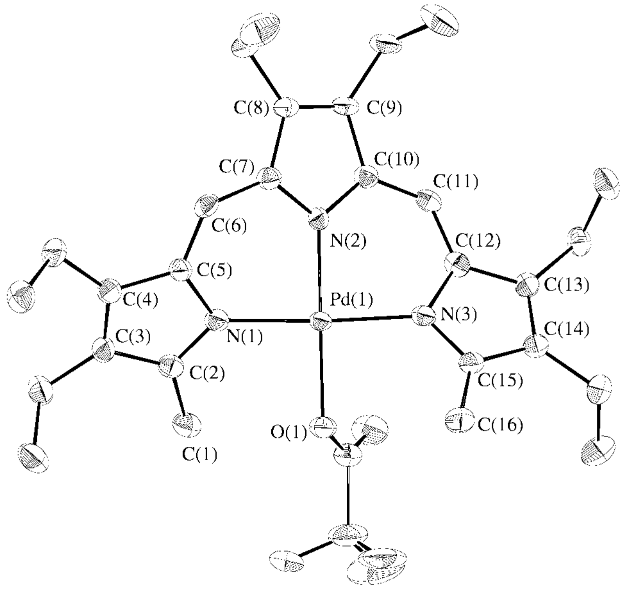


Fig. 1 ORTEP plot of the molecular structure of **7** (top view of molecule I). Selected bond lengths, distances (Å) and bond angles (°): Pd(1)–N(1) 2.026(4), Pd(1)–N(2) 1.973(3), Pd(1)–N(3) 2.021(3), Pd(1)–O(1) 2.051(2), C(1)–O(1) 2.942, C(16)–O(1) 2.980, C(1)–C(16) 5.919; N(1)–Pd(1)–N(2) 88.43(13), N(2)–Pd(1)–N(3) 88.27(12), N(1)–Pd(1)–N(3) 176.69(11), N(1)–Pd(1)–O(1) 91.92(12), N(2)–Pd(1)–O(1) 179.63(14), N(3)–Pd(1)–O(1) 91.38(12).

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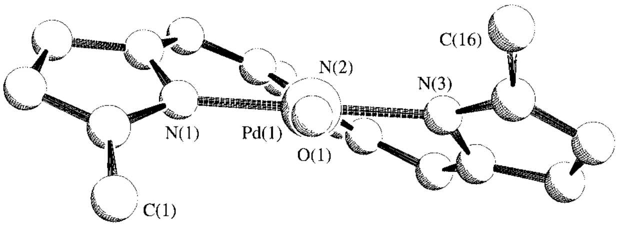

Fig. 2 Reduced view of the helical scaffolding pattern of **7** (Schakal plot, front view of molecule I).

Suitable crystals for X-ray diffraction were grown by slow evaporation of a solution of **7** in dichloromethane/*n*-hexane. Three independent molecules were found in the asymmetric unit, mainly differing from each other through the disordering pattern within the CF_3 group. In the following, only molecule I will be discussed. In the crystalline state, **7** is found to display a helically distorted and therefore chiral tripyrrin ligand with C_4N rings being tilted towards each other by 39.84 and 33.41°, respectively (Fig. 2). The unexpected and quite pronounced non-planarity of **7** appears in contrast to the effective C_{2h} symmetry observed by rt NMR and indicates a racemization process in solution, which is fast on the NMR time scale. The torsions observed in **7** parallel in part the out-of-plane distortion modes found for a number of metalloporphyrins.[11] Obviously, the non-planar structure is caused by the steric influence of the terminal methyl groups on the anionic ligand. Only by severely tilting the tripyrrin moiety, the binding oxygen atom O(1) of the trifluoracetate will find enough space to co-ordinate the central Pd ion within a square-planar geometry (distances C(1)–O(1) and C(16)–O(1): 2.942 and 2.980 Å). Whether the strain induced by the helical twist favours the dissociation of the trifluoroacetate and thus induces an enhanced reactivity of **7** and similar complexes, is currently under investigation.

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Notes and references

1 *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic, San Diego, CA, 2000.

2 H. Fischer and H. Orth, *Die Chemie des Pyrrols*, Akademische Verlagsgesellschaft m.b.H., Leipzig, 1940, vol. 2, erste Hälfte, p. 1–151; H. Falk, *The Chemistry of Linear Oligopyrroles and Bile Pigments*, Springer, Wien, 1989; C. Brückner, V. Karunaratne, S. J. Rettig and D. Dolphin, *Can. J. Chem.*, 1996, **74**, 2182.

3 K. M. Smith, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic, San Diego, CA, 2000, vol. 1, chapter 1, p. 1–44.

4 A better studied example from this class of ligands is bis(2-pyridylimino)isoindoline: J. A. Elvidge and R. P. Linstead, *J. Chem. Soc.*, 1952, 5000; M. A. Robinson, S. I. Trotz and T. J. Hurley, *Inorg. Chem.*, 1967, **6**, 392; W. O. Siegl, *Inorg. Chim. Acta*, 1977, **25**, L65; W. O. Siegl, *J. Heterocycl. Chem.*, 1981, **18**, 1613; R. R. Gagné, W. A. Marritt, D. N. Marks and W. O. Siegl, *Inorg. Chem.*, 1981, **20**, 3260.

5 J. L. Sessler, A. Gebauer, V. Král and V. Lynch, *Inorg. Chem.*, 1996, **35**, 6636.

6 F.-P. Montforts, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 778; F.-P. Montforts and U. M. Schwartz, *Liebigs Ann. Chem.*, 1985, 1228; D. Eichinger and H. Falk, *Monatsh. Chem.*, 1987, **118**, 261; R. G. Khoury, M. O. Senge, J. E. Colchester and K. M. Smith, *J. Chem. Soc., Dalton Trans.*, 1996, 3937; A. Jaumà, J.-A. Farrera and J. M. Ribó, *Monatsh. Chem.*, 1996, **127**, 936.

7 As judged by uv/vis and NMR spectra the major impurities consist of approx. 5% octaethylporphyrin and 10% dipyrrins.

8 *Spectroscopic data* for **6**: HRMS: *m*/*z* 419 ($[M - 2\ CF_3CO_2]^+$) $C_{28}H_{41}N_3$, calc. 419.330047, obs. 419.33031, Δ = 0.26 mmu; ^{1}H NMR (trifluoroacetic acid-d_1): δ = 7.32 (s, H_{meso}), 2.64 (q), 2.62 (q), 2.50 (br s), 2.41 (q), 1.12 (t), 1.07 (t), 1.01 (t); ^{13}C NMR (trifluoroacetic acid-d_1): δ = 173.4, 155.8, 144.9, 139.1, 137.0, 136.3 (6 × C_{quart}), 120.8 (C_{meso}), 18.8, 18.3, 17.7 (3 × CH_2CH_3), 16.1, 16.0, 13.6, 12.9 (4 × CH_3); uv/vis (trifluoroacetic acid): λ_{max}/nm 270 (ε_{rel} 0.06), 339 (0.18), 564 sh (0.19), 595 (0.28).

9 *Spectroscopic data* for **7**: mp 148 °C (decomp.); MS (EI, 70eV): *m*/*z* 521.3, $[M - CF_3CO_2]^+$; ^{1}H NMR (400 MHz, C_6D_6): δ= 6.70 (s, 2H, H_{meso}), 2.36 (q, 4H, CH_2CH_3), 2.31 (s, 6H, terminal CH_3), 2.21 (q, 4H, CH_2CH_3), 1.85 (q, 4H, CH_2CH_3), 1.04 (t, 6H, CH_2CH_3), 0.92 (t, 6H, CH_2CH_3), 0.75 (t, 6H, CH_2CH_3); ^{13}C NMR (100.6 MHz, C_6D_6): δ = 173.51, 161.97 [q, *J*(CF) = 34 Hz, CF_3CO_2], 147.85, 139.91, 137.18, 137.09, 128.29, 119.64 (C_{meso}), 116.36 [q, *J*(CF) = 390 Hz, CF_3CO_2], 18.11 (CH_2CH_3), 17.94 (2 × CH_2CH_3), 17.33, 16.88, 16.64, 14.33 (4 × CH_3); uv/vis (CH_2Cl_2): λ_{max}/nm 276 (ε 18 000), 358 (41 500), 637 sh (30 100), 684 (42 300); calc. for $C_{30}H_{38}F_3N_3PdO_2$: C 56.65, H 6.02, N 6.61; found: C 56.65, H 5.68, N 6.51%.

10 *Crystal data* for 3 × ($C_{30}H_{38}F_3N_3PdO_2$) **7**: violet cubes, *M* = 1908.10, triclinic, space group $P\bar{1}$, *a* = 13.168(3), *b* = 17.773(4), *c* = 20.929(4) Å, α = 73.83(3), β = 75.37(3), γ = 75.49(3)°, *U* = 4465.3(15) Å^3, *Z* = 2, D_c = 1.419 g cm^{-3}, μ = 0.673 mm^{-1}, *F*(000) = 1968, 37 922 reflections collected (2.41 < θ < 25.00°) at 173(2) K, 14 760 independent (R_{int} = 0.0637), 10 675 used in the structure refinement; R_1 = 0.0430 [$I > 2\sigma(I)$], wR_2 = 0.1062 (all data), GOF = 0.899 for 1159 parameters and 240 restraints, largest difference peak, hole = 1.496, −1.154 e Å^{-3}. CCDC 154850. See http://www.rsc.org/suppdata/cc/b0/b009847g/ for crystallographic files in .cif format.

11 M. O. Senge, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic, San Diego, CA, 2000, vol. 1, chapter 6, p. 239–347.