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One-step conversions of a simple corrole into chiral and amphiphilic derivatives

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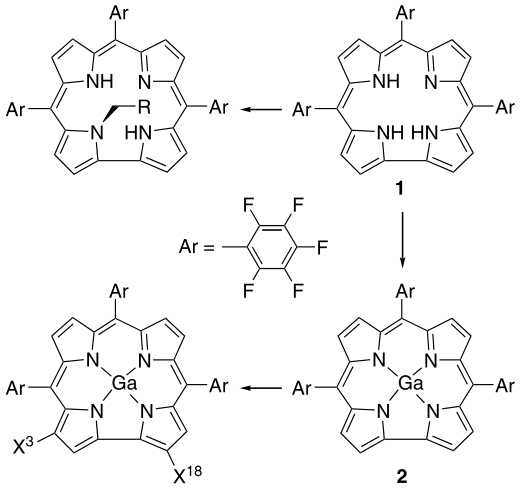
Abstract—The reactions of phosgene with 5,10,15-tris(pentafluorophenyl)corrole and its gallium(III) complex lead to a novel chiral macrocycle and an amphiphilic corrole, respectively. Both types of molecules were fully characterized by spectroscopy and X-ray crystallography.

Recent years have evidenced a renaissance in the chemistry of corroles,[1,2] due to the introduction of three facile synthetic methodologies for preparation of triarylcorroles: the solvent-free condensation of pyrrole and aldehydes,[3] the modified Rothemund procedure,[4] and the dipyrromethane condensation with aldehydes.[5] Among all new corroles, the *meso*-pentafluorophenyl substituted derivative (**1**, Scheme 1) is by far the most intensively studied. This single corrole and its variants have been shown to support a large variety of metal ions (Cr,[6] Mn,[7] Fe,[8] Ru,[9] Co,[10] Rh,[11] Ni,[12] Pd,[12] Cu,[12] Zn,[13] Al,[14] Ga,[15] Ge,[8b] Sn,[8b] P[8b]) and many of the complexes have been fully characterized in several oxidation and coordination states. The novel features that were disclosed for **1** and its metal complexes include very high fluorescence quantum yields,[14,15] potent catalytic activity,[6–8,16] and selective interactions with tumor cells.[17] In addition, facile methodologies for the functionalization of **1** were developed: alkylation of one of the nitrogen atoms leads to chiral corroles that can be separated into enantiomers and form coordination complexes with mono- and divalent metal ions;[11,13] amphiphilic corroles (and 'chiral metal' complexes) are obtained via substitution on the β-pyrrole carbon atoms of **1** or its gallium(III) complex (**2**), reactions that were demonstrated to proceed with extremely large selectivity.[18]

At first sight, the formylation products of **2** (**3** and **4** of Scheme 1) seem excellent precursors of the carboxylated corroles **5** and **6**, respectively. But, all attempts to convert **3** to **5** by applying standard procedures for oxidation of aldehydes to carboxylic acids failed. Apparently, this phenomenon is not unique to corroles: formylated tetraarylporphyrins were also reported most recently to be reluctant to oxidation.[19] Accordingly, we decided to look for an alternative route to **5** or **6**, compounds that are needed for our ongoing utilization of amphiphilic corroles in various applications.



3: X^3 = CHO, X^{18} = H
4: X^3 = X^{18} = CHO
5: X^3 = CO_2H, X^{18} = H
6: X^3 = X^{18} = CO_2H
10: X^3 = CO_2CH_3, X^{18} = H

Scheme 1.

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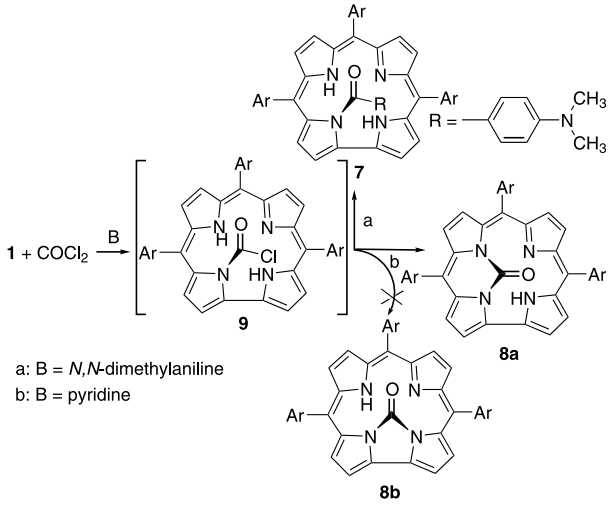
Based on the selective bis-substitution on C3 and C18 obtained with chlorosulfonic acid,[18] we decided to explore the reactivity of **1** toward phosgene. We did not expect problems from the reaction with the non-protected nitrogen atoms, since N-CO-R substituted corroles were reported to hydrolyze spontaneously.[20] However, the desired *C*-carboxylation did not occur and the only isolated material was compound **7** (Scheme 2), which contains the elements of *N*,*N*-dimethylaniline that was present for trapping the HCl released during reaction.[21] This unexpected product was avoided with pyridine as base, but carboxylation of the carbon atoms still did not occur. Instead, the novel compound **8a** was formed in very high yield.[22]

Apparently, the first product in both cases is the N-CO-Cl substituted corrole **9**, which subsequently reacts with either *N*,*N*-dimethylaniline via *C*-acylation or with an adjacent N atom of the corrole. The latter reaction was not reported for porphyrins, suggesting that the unique N_4 core of corroles is responsible for the phenomenon.[23] What is more, the other plausible carbamide product **8b** is not formed.

The distinction between **8a** and **8b** is straightforward, as the symmetry of the latter is higher and inconsistent with the ^{1}H and ^{19}F NMR spectra that display eight different β-pyrrole CH's (two of the doublets overlap) and three different *para*-F resonances (Fig. 1). What is more, compound **8a** (but not **8b**) has no element of symmetry, i.e. it is a chiral macrocycle. This is demonstrated by the HPLC chromatogram (Fig. 1c) obtained with the aid of a chiral stationary phase. Both the separated enantiomers and the racemic mixture were recrystallized to obtain X-ray quality crystals, which succeeded for the latter.[24]

The chiral molecular structure of **8a**, presented in Figure 2 for one of the enantiomers, disclosed the following characteristics. The corrole ring is severely twisted to avoid collision between the C=O group and the *N*-pyrrole proton. The former is oriented sharply upward, the dihedral angle between the N-CO-N plane



Scheme 2.

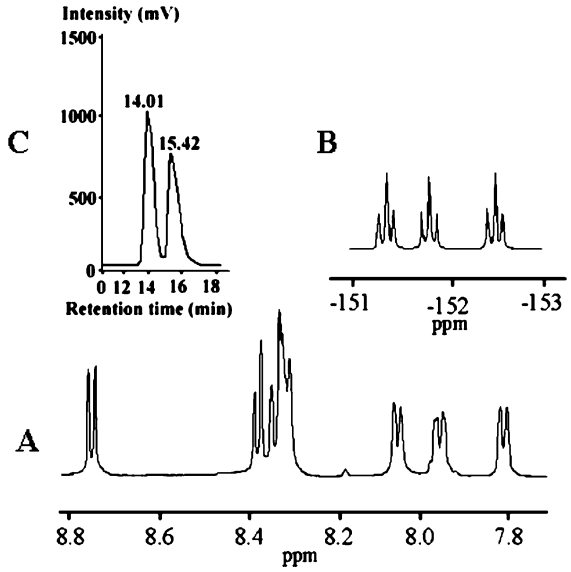


Figure 1. The (a) ^{1}H and (b) ^{19}F NMR spectra of compound **8a** and (c) the HPLC profile of its racemic mixture.

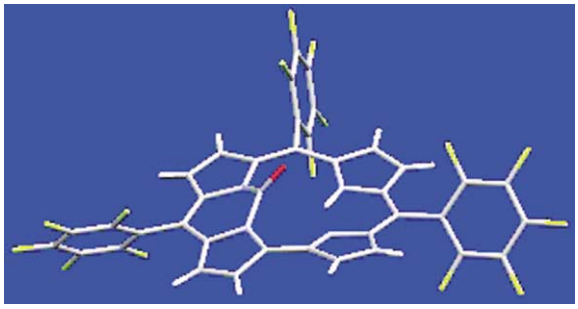


Figure 2. The molecular structure of **8a**.

and the neighboring pyrrole rings bridged by the carbonyl being 35 and 37°. In the resulting structure the *O*-atom lies 1.6 Å above the plane of the HN-pyrrole ring across the cavity. However, the observed CO···HN(pyrrole) nonbonding distance is still very short, 2.23(2) Å. An intramolecular H-bond between the protonated and unprotonated pyrrole rings is also evident in the structure: NH···N = 2.492(6) Å, H···N = 1.67 Å, and N–H···N = 143(1)°.

Based on the above results, the reaction of the gallium(III) complex **2** with phosgene was examined.[25] This approach was fruitful: the mono-carboxylated product **5** was isolated in 58% yield. Identification of **5** as the 3-substituted product (there are 3 other possibilities) is based on ^{1}H NMR spectroscopy, which is shown for its methyl ester, **10** (Fig. 3).[26] The presence of only two doublets with J <4.5 Hz is consistent with substitution on C2 or C3 and the chemical shift of the singlet (9.84 ppm) is distinct for C2H, as explained in detail for complex **3**.[18b]

This is further substantiated by the molecular structure of **5** (Fig. 4), for which X-ray quality crystals were obtained from a mixture of benzene and pyridine.[27]

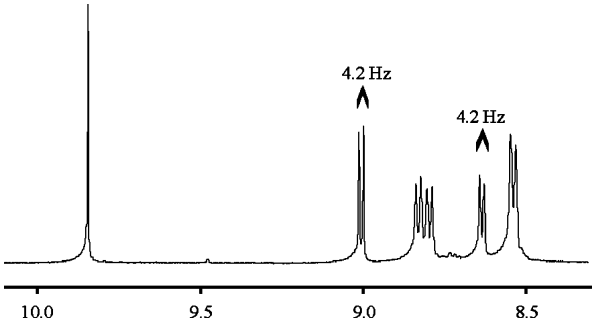


Figure 3. ^{1}H NMR spectrum of compound **10**.

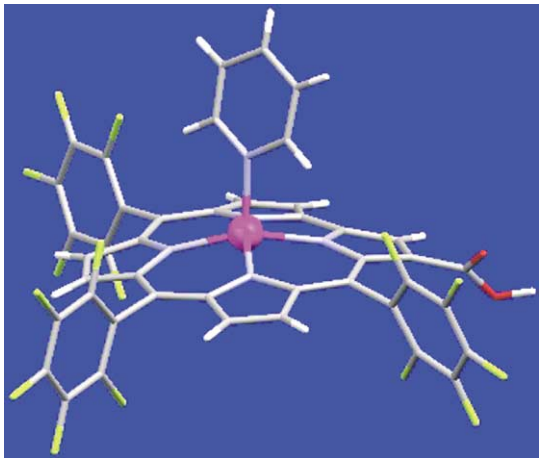


Figure 4. Molecular structure of **5**·pyridine.

Incidentally, the crystals were found to contain a single enantiomer of the chiral five-coordinate gallium complex, with an axial pyridine ligand bound to the metal center. Correspondingly, the complex has a domed structure, the gallium ion being displaced from the corrole plane towards the axial ligand, and the pyrrole rings being turned with their *N*-sites slightly upward. The four pyrrole *N*-atoms are displaced about 0.3 Å above the mean plane of the C_{19} carbon-only macrocycle. Then, the Ga(III) ion lies 0.4 Å above the N_4 plane. The Ga–N(pyrrole) and Ga–N(pyridine) bond lengths are 1.933–1.970(4) and 2.024(4) Å, respectively. The carboxylic group is aligned roughly parallel to the plane of the adjacent aryl substituent.

We have demonstrated that the unique N4 core in the free-base corrole **1** and the electron-richness of its gallium(III) complex **2** allow for the facile preparation of a chiral macrocycle and an amphiphilic corrole, respectively, via their direct reactions with phosgene.

Acknowledgements

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21. A 20% solution of phosgene (0.12 mL, 1.2 mmol) in toluene was added to a solution of **1** (0.096 g, 0.12 mmol) and *N*,*N*-dimethylaniline (0.029 g, 0.24 mmol) in toluene (7 mL) and stirred for 10 min at 0°C under an inert atmosphere, followed by heating for 4 h under reflux. The reaction was quenched with ice water and extracted with dichloromethane. The organic layer was washed with 10% citric acid and water three times, dried over anhydrous sodium sulfate, filtered and evaporated. The crude material was separated and purified via column chromatography (silica, hexane:ethyl acetate, 95:5 to 70:30), affording N^{21}-(4-*N*,*N*-dimethylaminobenzoyl)-5,10,15-tris(pentaflourophenyl)corrole (**7**, 36 mg, 32% yield) as violet crystals. R_f (silica, hexane:ethyl acetate, 1:1) = 0.4; ^{1}H NMR (C_6D_6): δ = 8.78 (d, ^3J(H,H) = 4.2 Hz, 1H), 8.61 (d, ^3J(H,H) = 4.8 Hz, 1H), 8.55 (d, ^3J(H,H) = 3.6 Hz, 2H), 8.43 (d, ^3J(H,H) = 4.8 Hz, 1H), 8.40 (d, ^3J(H,H) = 4.8 Hz, 1H), 8.27 (m, 2H), 7.57 (d, ^3J(H,H) = 8.7 Hz, 2H), 6.66 (d, ^3J(H,H) = 8.7 Hz, 2H), 2.41 (s, 6H); ^{19}F NMR (C_6D_6): δ = −138.16 (dd, ^3J(F,F) = 24.1 Hz, ^4J(F,F) = 7.5 Hz, 2F), −138.95 (m, 4F), −152.46 (t, ^3J(F,F) = 21.6 Hz, 1F), −152.94 (t, ^3J(F,F) = 22 Hz, 2F), −162.12 (m, 6F); UV–vis (EtOAc): λ_{max} 411 nm (ε 86,000), 568 (15,000), 609 (12,000); IR ($CHCl_3$, cm^{-1}): 1717 (CO); MS (DCI$^-$): *m*/*z* (%) 929 (100) $[M-CH_3]^-$.
22. A 20% solution of phosgene (0.12 mL, 1.2 mmol) in toluene was added to a solution of **1** (0.096 g, 0.12 mmol) and pyridine (0.02 g, 0.24 mmol) in toluene (7 mL) and stirred for 10 min at 0°C under an inert atmosphere, followed by heating for 15 min under reflux. The reaction was quenched with ice and water and extracted with dichloromethane. The organic layer was washed with water three times, dried over anhydrous sodium sulfate, filtered and evaporated. Flash column chromatography (silica, hexane:ethyl acetate, 95:5) afforded purple crystals of N^{21},N^{22}-carbamide-5,10,15-tris(pentafluorophenyl)-corrole (**8a**, 95 mg, 96% yield). R_f (silica, hexane: dichloromethane, 2:1) = 0.8; ^{1}H NMR (C_6D_6): δ = 8.74 (d, ^3J(H,H) = 4.7 Hz, 1H), 8.37 (d, ^3J(H,H) = 4.5 Hz, 1H), 8.31 (m, 3H), 8.06 (d, ^3J(H,H) = 4.5 Hz, 1H), 7.96 (d, ^3J(H,H) = 4.5 Hz, 1H), 7.81 (d, ^3J(H,H) = 4.5 Hz, 1H); ^{19}F NMR (C_6D_6): δ = −134.87 (d, ^3J(F,F) = 23.3 Hz, 1F), −137.83 (dd, ^3J(F,F) = 23.3 Hz, ^4J(F,F) = 5.6 Hz, 1F), −138.78 (m, 4F), −151.32 (t, ^3J(F,F) = 21.8 Hz, 1F), −151.77 (t, ^3J(F,F) = 21.8 Hz, 1F), −152.45 (t, ^3J(F,F) = 21.8 Hz, 1F), −160.66 (m, 2F), −161.40 (m, 3F), −161.89 (m, 1F); UV–vis (EtOAc): λ_{max} 401 nm (ε 65,700), 416 (47,900), 498 (4,400), 533 (7,200), 611 (3,700); IR ($CHCl_3$, cm^{-1}): 1749 (CO); MS (DCI$^-$): *m*/*z* (%): 822.0 (100). Separation of **8a** into its enantiomers was achieved by HPLC on Chiralcel OD.[14]
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24. Crystal data of **8a** (crystallized as dichloromethane di-solvate): $C_{38}H_9F_{15}N_4O{\cdot}2CH_2Cl_2$, formula weight 992.34, monoclinic, space group $P2_1/n$, a = 13.4400(2), b = 14.0110(2), c = 21.0710(4) Å, β = 102.384(1)°, V = 3765.33(11) Å^3, Z = 4, T = 110 K, D_{calcd} = 1.751 g cm^{-3}, 8446 unique reflections ($2\theta_{max}$ = 55.7°). The final R_1 = 0.076 for 5861 observations with $F_o > 4\sigma(F_o)$, R_1 = 0.109 (wR_2 = 0.241) for all unique data, $|\Delta\rho| \leq 1.26$ e Å^3 (near the partly disordered dichloromethane solvent). The *N*-pyrrole proton was located in residual electron-density maps. CCDC 210816.
25. A 20% solution of phosgene (0.12 mL, 1.2 mmol) in toluene (0.6 mL) was added dropwise (15 min) to an ice-cold solution of **2** (0.115 g, 0.12 mmol) and pyridine (0.02 g, 0.24 mmol) in toluene (7 mL), during which the solution turned from red to deep green. After stirring at 0–5°C for 30 min and at rt for 1 h, the reaction was quenched with ice water and extracted with dichloromethane. The organic layer was washed with water three times, dried over anhydrous sodium sulfate, filtered and evaporated. Separation from bis-substituted products (**6** and isomers thereof) via column chromatography (silica gel, hexane:ethyl acetate:pyridine, gradually changing from 95:5:0.2 to 25:75:0.2), afforded 3-carboxylate-5,10,15-tris(pentafluorophenyl)corrolato gallium(III)-(pyridine) (**5**, 69 mg, 58% yield) as blue–red crystals. R_f (silica, hexane:ethylacetate, 3:2) = 0.53; ^{1}H NMR (C_6D_6): δ = 10.09 (s, 1H), 8.91 (d, ^3J(H,H) = 3.8 Hz, 1H), 8.83 (d, ^3J(H,H) = 4.4 Hz, 1H), 8.75 (d, ^3J(H,H) = 4.1 Hz, 1H), 8.57 (d, ^3J(H,H) = 3.5 Hz, 1H), 8.52 (t, ^3J(H,H) = 4.0 Hz, 2H), 5.31 (t, ^3J(H,H) = 6.9 Hz, 1H), 4.77 (m, 2H), 3.9 (m, 2H); ^{19}F NMR (C_6D_6): δ = −138.82 (d, ^3J(F,F) = 24.1 Hz, 4F), −139.96 (dd, ^3J(F,F) = 24.1 Hz, ^4J(F,F) = 5.6 Hz, 2F), −152.94 (td, ^3J(F,F) = 20.5 Hz, ^4J(F,F) = 6.7 Hz, 2F), −155.6 (t, ^3J(F,F) = 21 Hz, 1F), −162.2 (m, 4F), −164.8 (t, ^3J(F,F) = 20.5 Hz, 2F); UV–vis (EtOAc): λ_{max} 404 nm (ε 37,000), 426 (130,000), 587 (18,000), 606 (21,000); IR ($CHCl_3$, cm^{-1}): 1720 (CO); MS (DCI$^-$): *m*/*z* (%) 906 (20) [M−pyridine]$^-$, 861.9 (100) [M$^-$−COOH].
26. A MeOH solution (7 mL) of **5** (59 mg, 0.06 mmol) and *N*,*N*-dimethylethylpropylcarbodiimide hydrochloride (12

mg, 0.06 mmol) were mixed overnight at room temperature, after which the solvent was evaporated. Column chromatography (silica, 8% ethyl acetate in hexane), provided 3-methylcarboxylate-5,10,15-tris(pentafluorophenyl)corrolato gallium(III)(pyridine) (**10**, 56 mg, 93% yield) as purple crystals. R_f (silica, hexane:ethyl acetate, 3:1) = 0.6; ^{1}H NMR (C_6D_6): δ = 9.84 (s, 1H), 9.01 (d, ^3J(H,H) = 4.2 Hz, 1H), 8.83 (d, ^3J(H,H) = 4.5 Hz, 1H), 8.78 (d, ^3J(H,H) = 4.8 Hz, 1H), 8.64 (d, ^3J(H,H) = 4.2 Hz, 1H), 8.54 (d, ^3J(H,H) = 4.5 Hz, 2H), 4.98 (t, ^3J(H,H) = 6.9 Hz, 1H), 4.40 (m, 2H), 3.70 (s, 3H), 2.9 (m, 2H); ^{19}F NMR (C_6D_6): δ = −138.86 (m, 4F), −140.36 (m, 2F), −152.40 (t, ^3J(F,F) = 20.9 Hz, 1F), −152.88 (t, ^3J(F,F) = 21.0 Hz, 1F), −155.34 (t, ^3J(F,F) = 20.9 Hz, 1F), −162.25 (m, 4F), −164.94 (m, 2F); UV–vis (EtOAc): λ_{max} 405 nm (ε 33,000), 425 (110,000), 592 (16,000), 609 (19,000); MS (DCI$^-$): m/z (%): 920 [M−pyridine]$^-$.

27. Crystal data of **5** (crystallized as benzene and pyridine solvate): $C_{43}H_{13}F_{15}GaN_5O_2 \cdot C_6H_6 \cdot C_5H_5N$, formula weight 1143.51, tetragonal, space group $P4_32_12$, a = 13.0570(4), c = 52.5570(13) Å, V = 8960.2(4) Å^3, Z = 8, T = 110 K, D_{calcd} = 1.695 g cm^{-3}, 8095 unique reflections ($2\theta_{max}$ = 50.7°). The final R_1 = 0.064 for 4435 observations with $F_o > 4\sigma(F_o)$, R_1 = 0.145 (wR_2 = 0.106) for all unique data, $|\Delta\rho| \leq 0.42$ e Å^3. The carboxyl proton was located on a difference-Fourier map. The carboxyl group is not involved in H-bonding due to a sterically hindered environment. CCDC 210815.