Demetalation of Copper Undecaarylcorroles: Molecular Structures of a Free-Base Undecaarylisocorrole and a Gold Undecaarylcorrole

Jan Capar,^a Job Zonneveld,^a Steffen Berg,^a Johan Isaksson,^a Kevin J. Gagnon,^b
Kolle E. Thomas,*^a and Abhik Ghosh*^a

^a Department of Chemistry and Center for Theoretical and Computational Chemistry, University of Tromsø, N-9037 Tromsø, Norway; Email: thomas.kolle@uit.no; abhik.ghosh@uit.no; ^b Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720-8229

Abstract. Copper undecaarylcorroles were found to undergo acid-induced demetalation with unusual ease under both reductive and nonreductive conditions. The resulting free-base undecaarylcorroles were found to be rather reactive, readily photooxygenating to yield 5/10-hydroxyisocorroles and open-chain tetrapyrroles. The use of nonreductive conditions led to fairly good yields of undecaarylisocorroles, a new class of sterically hindered ligands, of which one proved amenable to single-crystal X-ray structural analysis. In one case, interaction of an undecaarylisocorrole with gold(III) acetate resulted in aromatization of the macrocycle and a gold undecaarylcorrole. The Au complex exhibited Au-N distances of 1.941(3)-1.965(3) Å, and no significant nonbonded interactions involving the gold. The significant solubility of this complex in organic solvents, compared with the relative insolubility of gold β -octabromo-*meso*-triarylcorroles, appears to be related to the lack of aurophilic and metallophilic interactions.

Introduction. Metallocorroles,^[1,2,3,4] particularly copper corroles, are typically much more readily functionalized and elaborated in a controlled manner than free-base corroles. Subsequent demetalation then has the potential to yield novel, substituted free-base corrole ligands. Unfortunately, the demetalation of metallocorroles is generally more difficult than that of common metalloporphyrins, requiring both strong acid and an excess of a reductant such as a Fe(II) or Sn(II) salt.^[5,6,7,8,9,10] A notable success of this ‘reductive demetalation’ approach has been the synthesis of free-base β -octabromocorroles^[7,6,9,11] and their subsequent use as ligands.^[12,13,14] Here we report that copper undecaarylcorroles^[15,16,17] demetalate with unusual ease, in a matter of minutes, on exposure to acid, under both reductive and nonreductive conditions.

In what initially appeared to be a setback, free-base undecaarylcorroles were found to be rather reactive, readily reacting with ambient oxygen to generate 5-hydroxy- and 10-hydroxy-undecaarylisocorroles as well as open-chain dioxo compounds. As shown in Figure 1, isocorroles are fascinating ligands in their own right: they are porphyrin-like by virtue of their diprotic or dianionic character and corrole-like in affording a spatially constricted cavity for metal coordination.^[18,19,20,21,22] They are thus promising platforms for unusual transition metal spin states. In a pertinent study, Bröring and coworkers have reported that thiacorroles, which are structurally similar to isocorroles, give rise to intermediate-spin iron(III) complexes.^[23] A second remarkable feature of isocorroles is their strong absorption in the near-infrared,^[21] which is of great relevance to photodynamic therapy.^[24] Reported herein are optimized syntheses for a family of sterically hindered undecaarylisocorrole ligands, including the first, single-crystal X-ray structure of a free-base undecaarylisocorrole.

Furthermore, we have attempted to determine whether undecaarylisocorrole ligands can be rearomatized on metal complexation, yielding novel undecaarylcorrole complexes. This is an important question because, as of today, only copper and cobalt undecaarylcorroles have been reported.^[15-17] New metalloundecaarylcorroles are of considerable interest as shape-selective catalysts and other functional materials. As shown in Figure 2, we found that at least one free-base undecaarylisocorrole could be smoothly converted to the corresponding gold undecaarylcorrole. The same gold complex could also be obtained from a gold β -octabromo-*meso*-triarylcorrole via a tedious, week-long Suzuki coupling procedure. Remetalation and aromatization of isocorroles to corroles, when feasible, thus promises to be a useful transformation.

Figure 1. Steric and electronic relationships between porphyrin, corrole, and isocorrole ligands. Whereas porphyrin and isocorroles share the same proticity (both coordinate as dianionic ligands), isocorroles and corroles share similar, constricted coordination cavities.

Figure 2. Two alternative synthetic routes to the gold undecaarylcorrole $\text{Au}[(\text{CF}_3)_8\text{H}_3]$.

Results and Discussion

(a) **Demetalation of copper undecaarylcorroles and isocorrole formation.** Four different copper undecaarylcorroles were demetallated in this study, copper β -octakis(*p*-X-phenyl)-*meso*-tris(*p*-methylphenyl)corrole, where X = H, F, and CF₃, and copper β -octakis(*p*-trifluoromethylphenyl)-*meso*-triphenylcorrole (Figure 3). For brevity, we will refer to these complexes as Cu[X₈Me₃]. We will also refer to the corresponding free-base corroles as H₃[X₈Me₃] and the isocorroles as H₂[X₈Me₃(5-OH)]. Reductive demetalation of Cu[X₈Me₃] with concentrated sulfuric acid and ~10 equiv of anhydrous FeCl₂ led to ~70% yields of the free-base corroles, H₃[X₈Me₃], in a matter of minutes, but in the presence of air and light, free-base undecaarylcorroles quickly decomposed to open-chain dioxotetrapyrroles and small quantities of the isocorroles, H₂[X₈Me₃(5/10-OH)]. Eliminating reductive conditions (i.e., FeCl₂) proved to be an effective way of improving the yield of isocorroles, the key targets of this study, as did the presence of an organic solvent such as dichloromethane. The final optimized conditions, involving demetalation in dichloromethane and concentrated sulfuric acid, led to 50-65% yields of highly stable, free-base isocorroles, with negligible quantities of corroles and open-chain tetrapyrroles.

Figure 3. Corrole and isocorrole derivatives investigated in this study.

Each demetalation led to both 5- and 10-OH isocorroles, with the former dominating. Although not separable by column chromatography, the two regioisomers could be separated by preparative thin-layer chromatography. Except for one case, $\text{H}_2[(\text{CF}_3)_8\text{Me}_3(10\text{-OH})]$, however, the pure 10-regioisomer was not obtained in large enough quantities for full characterization. Figure 4 presents the UV-vis absorption spectra of these two isomeric compounds; note the intense Soret-like features, despite the lack of aromaticity, and strong absorption in the red and near-infrared. Examples of preferential formation of one or the other regioisomer well-documented in the literature.^[25,26,27] Thus, a convenient isocorrole synthesis, involving DDQ oxidation of *meso*-triarylcorroles in methanol, was found to lead preferentially to 5-OMe isocorroles.^[22] On the other hand, nonreductive demetalation of $\text{Cu}[\text{Br}_8\text{H}_3]$ (i.e., copper β -octabromo-*meso*-triphenylcorrole) with $\text{H}_2\text{SO}_4/\text{CHCl}_3$ led to preferential formation of the 10-OH isocorrole, $\text{H}_2[\text{Br}_8\text{H}_3(10\text{-OH})]$.^[5] A combination of electronic and steric factors is presumably responsible for the preponderance of one isomer over the other.

Figure 4. UV-vis spectra of $\text{H}_2[(\text{CF}_3)_8\text{H}_3(5\text{-OH})]$ and $\text{H}_2[(\text{CF}_3)_8\text{H}_3(10\text{-OH})]$.

Literature reports suggest that the oxygen in 5/10-OH isocorroles arises from O_2 rather than water, although the latter has not been strictly ruled out.^[26,27] To determine the source of oxygen in the isocorroles obtained in this study, we carried out isotope labeling experiments with H_2^{18}O and $^{18}\text{O}_2$. The freshly purified, vacuum-dried corrole $\text{H}_3[(\text{CF}_3)_8\text{Me}_3]$, upon stirring in anhydrous dichloromethane and H_2^{18}O under argon, showed no evidence of ^{18}O incorporation with electrospray ionization (ESI) mass spectrometry (MS). In contrast, bubbling $^{16}\text{O}_2$ into a solution of pure $\text{H}_3[(\text{CF}_3)_8\text{Me}_3]$ in anhydrous dichloromethane revealed the incorporation of both

one and two oxygen atoms via ESI-MS. Flushing the ESI mass spectrometer with $^{18}\text{O}_2$ also resulted in the incorporation of both one and two ^{18}O atoms into $\text{H}_3[(\text{CF}_3)_8\text{Me}_3]$, confirming the strong affinity of free-base undecaarylcorroles for dioxygen. One plausible pathway for the oxidative decomposition of free-base corroles, based on both literature precedence^[26,27,28,29] and our own experiments, is depicted in Figure 5.

Figure 5. Proposed pathway for photooxygenation of a free-base undecaarylcorrole. Analogous mechanisms can be drawn for O_2 attack at the 2- and 10- positions.

A single-crystal X-ray structure could be obtained for the free-base undecaarylisocorrole $\text{H}_2[(\text{CF}_3)_8\text{Me}_3(5\text{-OH})]$ (Figure 6, Table 1). Despite the considerable steric crowding, the macrocyclic skeleton of $\text{H}_2[(\text{CF}_3)_8\text{Me}_3(5\text{-OH})]$ was found to be essentially planar, as for other free-base isocorroles, but in sharp contrast to free-base corroles, which are generally strongly buckled as a result of steric repulsion among the three inner hydrogens.^[30,31] The two central hydrogens of $\text{H}_2[(\text{CF}_3)_8\text{Me}_3(5\text{-OH})]$ could be unambiguously located from the difference map. The skeletal bond distances, which are broadly similar to those observed for other 5-isocorrole structures,^[21,25] are consistent with strong localization of single and double bonds, with no significant indication of homoaromaticity.

Table 1. Crystallographic data for $\text{H}_2[(\text{CF}_3)_8\text{Me}_3(5\text{-OH})]$.

Sample	$\text{H}_2[(\text{CF}_3)_8\text{Me}_3(5\text{-OH})]$	$\text{Au}[(\text{CF}_3)_8\text{H}_3]$
Chemical formula	$\text{C}_{96}\text{H}_{56}\text{F}_{24}\text{N}_4$	$\text{C}_{95}\text{H}_{51}\text{F}_{24}\text{N}_4\text{Cl}_4\text{Au}$
Formula mass	1737.44	2043.16
Crystal system	Triclinic	Triclinic
Space group	$P\ 1$	$P\ -1$
λ (Å)	0.7749	0.7749
a (Å)	12.783(3)	15.4998(6)
b (Å)	18.085(4)	16.8410(6)
c (Å)	18.600(4)	16.9639(6)
α (deg.)	102.363(3)	106.229(2)
β (deg.)	108.203(3)	91.961(2)
γ (deg.)	96.468(3)	106.901(2)
Z	2	2
V (Å ³)	3914.7(15)	4035.8(3)
Temperature (K)	100(2)	100(2)
Density (g/cm ³)	1.474	1.681
Measured reflections	40303	78866
Unique reflections	15237	29236
Parameters	1169	1256
Restraints	66	646
R_{int}	0.0670	0.0524
θ range (deg.)	2.587 – 28.553	2.165 – 36.007
R_1 , wR_2 all data	0.0683, 0.2226	0.0459, 0.1140
S (GooF) all data	1.024	1.030
Max/min res. Dens. (e/Å ³)	0.410/-0.349	2.151/-1.956

(b) Synthesis and molecular structure of a gold undecaarylcorrole. Given the oxidative instability of free-base undecaarylcorroles, we were intrigued by the question whether metal insertion into a free-base undecaarylisocorrole might proceed with concomitant aromatization, thereby providing a pathway to novel metalloundecaarylcorroles. Although a full exploration of this question, involving different isocorroles and metal ions, has not yet been carried out, we were gratified to discover that interaction of free-base $\text{H}_3[(\text{CF}_3)_8\text{H}_3(5\text{-OH})]$ and gold(III) acetate in pyridine leads to the fully aromatized undecaarylcorrole complex $\text{Au}[(\text{CF}_3)_8\text{H}_3]$ in yields of ~40%.^[32,33] We are currently examining the generality of this process and will report on our findings in due course.

Unlike many gold β -octabromocorrole complexes, which tend to be quite insoluble, presumably because of intermolecular metallophilic $\text{Au}\dots\text{Br}$ interactions,³² $\text{Au}[(\text{CF}_3)_8\text{H}_3]$ was

found to be moderately soluble. X-ray quality crystals were obtained and single-crystal structure determination revealed a planar Au corrole, Au-N distances of 1.941(3)-1.965(3) Å, and no significant nonbonded interactions involving the gold (Figure 6).^[34] The planarity of the gold corrole may be contrasted with the strong nonplanarity of copper corroles, which is believed to be due to ligand noninnocence. Silver corroles exhibit more variable behavior in this regard. Thus, whereas simple silver *meso*-triarylcorroles are only slightly saddled,^[35] a recent X-ray structure has provided an example of a strongly saddled silver β -octabromocorrole.^[36] The substantial variations in corrole geometry in the silver case have been attributed to variations in noninnocent character among the different ligands. By contrast, corrole ligands in gold corroles are thought to be innocent.

Figure 7. X-ray structure of the gold undecaarylcorrole Au[(CF₃)₈H₃]: (a) top view and (b) side view.

Conclusion

In summary, copper undecaarylcorroles were found to demetallate with unusual ease under standard reductive demetalation conditions. The free-base undecaarylcorroles, however, proved to be light- and oxygen-sensitive, readily oxidizing to open-chain dioxotetrapyrroles and 5/10-OH isocorroles. Nonreductive conditions could be devised that led to good yields 65-80% of 5/10-OH undecaarylisocorroles, a new class of sterically hindered and relatively stable macrocyclic ligands. Interaction of one such ligand with gold(III) acetate resulted in rearomatization of the macrocycle and a gold undecaarylcorrole, which proved amenable to single-crystal X-ray diffraction analysis. Unlike the rather insoluble gold β -octabromo-*meso*-triarylcorroles, the gold undecaarylcorrole was found to be moderately soluble in organic solvents. The relatively high solubility appears to be related to the lack of intermolecular aurophilic and metallophilic interactions involving the gold atom.

Experimental section

Materials. All reagents and solvents were used as purchased unless stated otherwise. Anhydrous toluene (Sigma-aldrich) was stored over pre-activated 3 Å molecular sieves. Silica gel 150 (35-70 μ m particle size, Davisil) was used for flash chromatography and silica gel 60 plates (20 $\times$ 20 cm; 0.5 mm thick, Merck) were used for preparative thin-layer chromatography (PLC). Copper β -octabromo-*meso*-tris(4-methylphenyl)corrole, Cu[Br₈Me₃] and copper β -octabromo-*meso*-triphenylcorrole, Cu[Br₈H₃], served as the starting materials for copper undecaarylcorroles and were synthesized as previously described.^[37] Copper β -octakis(*p*-trifluoromethylphenyl)-*meso*-triphenylcorrole], Cu[(CF₃)₈H₃], was also synthesized according to a literature method.^[15]

Instrumentation. Ultraviolet-visible (UV-vis) spectra were recorded with CH₂Cl₂ as solvent on an HP 8453 spectrophotometer. ¹H NMR spectra were obtained at 298 K on either a Mercury Plus Varian spectrometer (400 MHz) in CDCl₃ (referenced to 7.26 ppm), in CD₂Cl₂ (referenced to 5.30 ppm), and in C₆D₆ (referenced to 7.20 ppm) or a Varian Inova spectrometer (600MHz) equipped with a cryogenically cooled inverse triple-resonance probe in 1,1,2,2-tetrachloroethane-*d*₂ (CDCl₂-CDCl₂, referenced to 5.91ppm). ¹⁹F NMR spectra (376 MHz) were recorded at 298-333K on a Mercury Plus Varian spectrometer and referenced to 2,2,2-trifluoroethanol-*d*₃ (δ = -77.8 ppm). Electrospray ionization mass spectra were recorded on an LTQ Orbitrap XL spectrometer.

General Procedure for the Synthesis of Copper Undecaarylcorroles. The syntheses were carried essentially according to the procedure reported by Ghosh and coworkers.^[15] Into a 50-mL three-necked round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser were introduced Cu[Br₈Me₃], the arylboronic acid of choice (40 equiv), potassium carbonate (40 equiv), and Pd₂(dba)₃·CHCl₃ (0.1 equiv). After degassing with argon, dry toluene (10 mL) was added. After purging with argon for 10 min, the suspension was stirred at 100–105 °C under argon for 1–2 days. Progress of the reaction was monitored by mass spectrometry. When product formation appeared to have stabilized, the reaction mixture was cooled to room temperature, diluted with 10 mL of CH₂Cl₂, and washed with saturated aqueous NaHCO₃ and then with distilled water. The CH₂Cl₂ phase was dried with anhydrous Na₂SO₄, filtered, and evaporated. The brown residue obtained was chromatographed on a silica gel column with hexane/CH₂Cl₂ as eluent. The product eluted as a dark brown band, which was collected and evaporated to dryness. The residue was purified by preparative thin-layer chromatography (PLC), as detailed below for each corrole.

Synthesis of Copper 2,3,7,8,12,13,17,18-octakis(4-fluorophenyl)-meso-tris(*p*-methylphenyl)corrole, Cu[F₈Me₃]. The reaction employed 0.025 mol (32 mg) of Cu[Br₈TMePC] and was complete after ~2 days (45 h). Both the column chromatography and subsequent PLC were carried out with 3:1 hexane/CH₂Cl₂ as eluent. The pure product Cu[F₈Me₃] (26.6 mg, 76%) eluted as the most intense brown band. UV-vis (CH₂Cl₂): λ_{max}, nm (ε x 10⁻⁴, M⁻¹ cm⁻¹): 448 (3.56), 644 (0.32). ¹H NMR (CDCl₃, 400 MHz, δ in ppm): δ 6.87 (d, *J*=8.0 Hz, 2H, 10-*o*, 4-CH₃Ph), 6.80-6.74 (m, 4H, 2,18-*o*, 4-FPh; 4H, 5,15-*o*, 4-CH₃Ph), 6.57-6.51 (m, 4H, 3,17-*o*, 4-FPh; 4H, 2,18-*m*, 4-FPh), 6.47-6.26 (m, 4H, 8,12-*o*, 4-FPh; 4H, 7,13-*o*, 4-FPh; 4H, 3,17-*m*, 4-FPh; 4H, 5,15-*m*, 4-CH₃Ph; 4H, 7,13-*m*, 4-FPh; 4H, 8,12-*m*, 4-FPh; 2H, 10-*m*, 4-CH₃Ph), 2.02 (s, 6H, 5,15-*p*, 4-CH₃Ph), 1.91 (s, 3H, 10-*p*, 4-CH₃Ph). ¹⁹F NMR (CDCl₃): δ -116.31 to -116.39 (m, 2F), -118.08 to -118.21 (m, 4F), -118.62 to -118.70 (m, 2F). MS (HR-ESI, major isotopomer): [M]⁺ = 1380.3440 (expt), 1380.3438 (calcd).

Synthesis of Copper 2,3,7,8,12,13,17,18-Octakis(4-trifluoromethylphenyl)-5,10,15-tris(4-methylphenyl)corrole, Cu[(CF₃)₈Me₃]. The reaction employed 0.020 mol (25 mg) of Cu[Br₈TMePC] and was complete after 24 h. Both the column chromatography and subsequent PLC were carried out with 3:1 hexane/CH₂Cl₂ as eluent. The pure product Cu[(CF₃)₈Me₃] (18.4 mg, 52%) eluted as the most intense brown band. UV-vis (CH₂Cl₂): λ_{max}, nm (ε x 10⁻⁴, M⁻¹ cm⁻¹): 454 (4.34), 642 (0.44), 841 (0.59). ¹H NMR (CDCl₃, 600 MHz, δ in ppm): δ 7.09 (d, *J*=4.0 Hz,

4H, 2,18-*o*, 4-CF₃Ph), 6.97 (d, *J*=4.0 Hz, 4H, 2,18-*m*, 4-CF₃Ph), 6.94 (d, *J*=4.0 Hz, 4H, 3,17-*o*, 4-CF₃Ph), 6.89 (d, *J*=4.0 Hz, 4H, 7,13-*o*, 4-CF₃Ph), 6.85 (d, *J*=4.0 Hz, 4H, 8,12-*o*, 4-CF₃Ph), 6.81 (d, *J*=8.0 Hz, 2H, 10-*o*, 4-CH₃Ph), 6.75 (d, *J*=4.0 Hz, 4H, 3,17-*m*, 4-CF₃Ph), 6.69 (d, *J*=8.0 Hz, 4H, 5,15-*o*, 4-CH₃Ph), 6.62 (d, *J*=8.0 Hz, 8H, 7,8,12,13-*m*, 4-CF₃Ph), 6.25 (d, *J*=4.0 Hz, 4H, 5,15-*m*, 4-CH₃Ph), 6.19 (d, *J*=8.0 Hz, 2H, 10-*m*, 4-CH₃Ph), 1.93 (s, 6H, 5,15-*p*, 4-CH₃Ph), 1.82 (s, 3H, 10-*p*, 4-CH₃Ph). ¹⁹F NMR (CDCl₃): δ -63.07 (s, 6F), -63.17 (s, 6F), -63.29 (s, 6F), -63.46 (s, 6F). MS (HR-ESI, major isotopomer): [M]⁺ = 1781.3211 (expt), 1781.3261 (calcd).

Synthesis of Copper 2,3,7,8,12,13,17,18-octaphenyl-5,10,15-tris(4-methylphenyl)corrole, Cu[H₈Me₃]. The reaction employed 0.021 mol (27 mg) of Cu[Br₈TMePC] and was complete after 48 h. Column chromatography was carried out with hexane/CH₂Cl₂ as eluent, while 3:1 *n*-hexane/CH₂Cl₂ was used for the PLC. The pure product Cu[H₈Me₃] (12.1 mg, 46%) eluted as the most intense brown band. UV-vis (CH₂Cl₂): λ_{max}, nm (ε x 10⁻⁴, M⁻¹ cm⁻¹): 448 (6.17), 544 (0.77), 645 (0.49). ¹H NMR (CD₂Cl₂, 600 MHz, δ in ppm): δ 6.86 (d, *J*=8.4 Hz, 2H, 10-*o*, 4-CH₃Ph), 6.85-6.82 (m, 4H, 2,18-*o*, Ph; 2H, 2,18-*p*, Ph), 6.80-6.76 (m, 4H, 2,18-*m*, Ph), 6.74 (d, *J*=7.8 Hz, 4H, 5,15-*o*, 4-CH₃Ph), 6.72-6.68 (m, 2H, 3,17-*p*, Ph), 6.65-6.63 (m, 4H, 3,17-*o*, Ph; 4H, 3,17-*m*, Ph), 6.62-6.58 (m, 2H, 7,13-*p*, Ph; 4H, 7,13-*m*, Ph), 6.58-6.57 (m, 2H, 8,12-*p*, Ph), 6.57-6.54 (m, 4H, 8,12-*m*, Ph; 4H, 8,12-*o*, Ph), 6.54-6.52 (m, 4H, 7,13-*o*, Ph), 6.19 (d, *J*=7.2 Hz, 4H, 5,15-*m*, 4-CH₃Ph), 6.16 (d, *J*=7.8 Hz, 2H, 10-*m*, 4-CH₃Ph), 1.90 (s, 6H, 5,15-*p*, 4-CH₃Ph), 1.80 (s, 3H, 10-*p*, 4-CH₃Ph). MS (HR-ESI, major isotopomer): [M]⁺ = 1237.4223 (expt), 1237.4220 (calcd).

Undecaarylisorrole H₂[F₈Me₃(5-OH)]. Into a 50 mL round-bottomed flask was placed 25 mg (0.018 mmol) of Cu[F₈Me₃] and dissolved in 3 mL of CH₂Cl₂. Subsequently, 3 mL of concentrated H₂SO₄ (95-97%, Merck) was added. The mixture was then stirred and sonicated at room temperature. Progress of the reaction was monitored by ESI mass spectrometry. After 2 h, the reaction mixture was carefully poured into 300 mL of distilled H₂O and then extracted with CHCl₃. The organic phase was washed once with distilled water and twice with saturated aqueous NaHCO₃. Upon washing with NaHCO₃, the color of the organic phase changed from brown to green. The organic phase was then dried with anhydrous Na₂SO₄, filtered, and the filtrate rotary-evaporated to dryness. The residue obtained was chromatographed on a silica gel column with CH₂Cl₂/1%-MeOH. The product was further purified by PLC with 2:3 *n*-hexane/CH₂Cl₂; upon completion of the PLC, the pure product H₂[F₈Me₃(5-OH)] (14.4 mg, 60%) was obtained as the most intense green band in the middle of the plate. UV-vis (CH₂Cl₂): λ_{max}, nm (ε x 10⁻⁴, M⁻¹ cm⁻¹

¹): 433 (3.37), 683 (0.69). ¹H NMR (C₆D₆, 600 MHz, δ in ppm): δ 8.05 (d, *J* = 8.1 Hz, 2H, 5-*o*, 4-CH₃Ph), 7.01 (d, *J* = 8.3 Hz, 2H, 5-*m*, 4-FPh), 6.81 (d, *J* = 8.1 Hz, 1H, 10-*o*, 4-CH₃Ph), 6.80 (d, *J* = 8.6 Hz, 2H, 3-*o*, 4-FPh), 6.70 (d, *J* = 8.0 Hz, 1H, 7-*o*, 4-FPh), 6.69 (t, *J* = 7.6 Hz, 1H, 7-*m*, 4-FPh), 6.60 (d, *J* = 8.6 Hz, 2H, 2-*o*, 4-FPh), 6.55 (t, *J* = 8.5 Hz, 2H, 3-*m*, 4-FPh), 6.44 (overlapping, 1H, 7-*o*, 4-FPh), 6.42 (o, 12-*o*, 4-FPh), 6.36 (o, 1H, 7-*m*, 4-FPh), 6.33 (o, 1H, 10-*m*, 4-CH₃Ph), 6.29 (o, 1H, 8-*m*, 4-FPh), 6.25 (t, *J* = 8.8 Hz, 2H, 2-*m*, 4-FPh), 6.20 (o, 1H, 8-*o*, 4-FPh), 6.11 (o, 1H, 8-*m*, 4-FPh), 6.07 (d, *J* = 8.4 Hz, 1H, 10-*o*, 4-CH₃Ph), 6.02 (t, *J* = 8.5 Hz, 0.5H, 12-*m*, 4-FPh), 5.65 (d, *J* = 7.8 Hz, 1H, 10-*m*, 4-CH₃Ph), 2.29 (s, 1H, -OH), 2.05 (s, 3H, 5-*p*, 4-CH₃Ph), 1.86 (s, 3H, 15-*p*, 4-CH₃Ph), 1.72 (s, 3H, 10-*p*, 4-CH₃Ph). ¹⁹F NMR (CDCl₃): δ -115.96 to -116.08 (m, 1F), -116.25 to -116.36 (m, 1F), -116.45 to -116.59 (m, 1F), -117.38 to -117.49 (m, 1F), -117.79 to -117.88 (m, 1F), -117.95 to -118.09 (m, 2F), -118.25 to -118.35 (m, 1F). MS (HR-ESI, major isotopomer): [M + H]⁺ = 1337.4415 (expt), 1337.4399 (calcd).

Undecaarylisocorroles H₂[(CF₃)₈Me₃(5-OH)] and H₂[(CF₃)₈Me₃(10-OH)]. Into a 50 mL round-bottomed flask, 20 mg (0.0112 mmol) of Cu[(CF₃)₈Me₃] was added and dissolved in 4 mL of CH₂Cl₂. Subsequently, 2 mL of concentrated H₂SO₄ (95-97%, Merck) was added. The mixture was stirred and sonicated at room temperature. The progress of the reaction was monitored by ESI mass spectrometry. After 4 hours the reaction was quenched by pouring the mixture into 300 mL distilled H₂O and then extracted with CHCl₃. The brown organic phase was washed once with distilled water and once with saturated aqueous NaHCO₃. Upon washing with NaHCO₃ the color of organic phase changed from brown to green. The organic phase was dried with anhydrous Na₂SO₄, filtered and evaporated under vacuum. The residue obtained was chromatographed on a silica gel column with 2:1 *n*-hexane/CH₂Cl₂. The product was further purified by PLC with 2:1 *n*-hexane/CH₂Cl₂. The most intense green band in the middle of the plate was pure H₂[(CF₃)₈Me₃(5-OH)] (11 mg, 57%) and the most intense light-green band below that was H₂[(CF₃)₈Me₃(10-OH)] (3.7 mg, 19%). X-ray quality crystals of H₂[(CF₃)₈Me₃(5-OH)] were grown by slow diffusion of *n*-heptane into the benzene solution. Analytical data for the two isomers are as follows.

Undecaarylisocorrole H₂[(CF₃)₈Me₃(5-OH)]. UV-vis (CH₂Cl₂): λ_{max}, nm (ε × 10⁻⁴, M⁻¹ cm⁻¹): 435 (4.19), 683 (0.92). ¹H NMR (C₆D₆, 600 MHz, δ in ppm): δ 7.95 (d, *J* = 8.0 Hz, 2H, 5-*o*, 4-CH₃Ph), 7.22 (d, *J* = 8.0 Hz, 1H, 7-*m*, 4-CF₃Ph), 7.05 (d, *J* = 8.0 Hz, 2H, 3-*m*, 4-CF₃Ph), 7.03 (d, *J* = 8.1 Hz, 2H, 5-*m*, 4-CH₃Ph), 6.87 (d, *J* = 7.9 Hz, 2H, 3-*o*, 4-CF₃Ph), 6.75 (d, *J* = 8.4 Hz, 1H, 7-*m*, 4-CF₃Ph), 6.72 (d, *J* = 8.0 Hz, 1H, 7-*o*, 4-CF₃Ph), 6.68 (o, 1H, 10-*o*, 4-CH₃Ph), 6.61 (d,

$J = 8.6$ Hz, 1H, 8-*m*, 4-CF₃Ph), 6.61 (o, 2H, 12-*m*, 4-CF₃Ph), 6.61 (o, 1H, 15-*m*, 4-CH₃Ph), 6.6 (o, 2H, 2-*m*, 4-CF₃Ph), 6.6 (o, 2H, 2-*o*, 4-CF₃Ph), 6.57 (o, 1H, 15-*m*, 4-CH₃Ph), 6.53 (d, $J = 8.2$ Hz, 1H, 8-*m*, 4-CF₃Ph), 6.44 (d, $J = 8.4$ Hz, 1H, 7-*o*, 4-CF₃Ph), 6.37 (broad, 1H, 15-*o*, 4-CH₃Ph), 6.35 (d, $J = 8.6$ Hz, 1H, 8-*o*, 4-CF₃Ph), 6.26 (b, 1H, 15-*o*, 4-CH₃Ph), 6.17 (d, $J = 7.9$ Hz, 1H, 10-*m*, 4-CH₃Ph), 6.13 (d, $J = 8.2$ Hz, 1H, 8-*o*, 4-CF₃Ph), 5.93 (d, $J = 7.8$ Hz, 1H, 10-*o*, 4-CH₃Ph), 5.48 (d, $J = 7.8$ Hz, 1H, 10-*m*, 4-CH₃Ph), 2.07 (s, 3H, 5-*p*, 4-CH₃Ph), 1.97 (s, 1H, -OH), 1.86 (s, 3H, 15-*p*, 4-CH₃Ph), 1.68 (s, 3H, 10-*p*, 4-CH₃Ph). ¹⁹F NMR (C₆D₆, 60°C): δ -62.58 (s, 3F), -62.72 (s, 9F), -62.88 (s, 3F), -62.95 (s, 3F), -63.06 (s, 3F), -63.32 (s, 3F). MS (HR-ESI, major isotopomer): $[M + H]^+ = 1738.4250$ (expt), 1738.4177 (calcd).

Undecaarylisorcorrole H₂[(CF₃)₈Me₃(10-OH)]. UV-vis (CH₂Cl₂): $\lambda_{\max}$, nm ($\epsilon \times 10^{-4}$, M⁻¹ cm⁻¹): 458 (1.86), 658 (0.26). ¹H NMR (C₆D₆, 600 MHz, δ in ppm): δ 7.46 (d, $J = 8.3$ Hz, 2H, 10-*o*, 4-CH₃Ph), 6.95 (d, $J = 8.1$ Hz, 4H, 12-*m*, 4-CF₃Ph), 6.80 (d, $J = 8.2$ Hz, 4H, 18-*m*, 4-CF₃Ph), 6.77 (d, $J = 8.1$ Hz, 2H, 10-*m*, 4-CH₃Ph), 6.72 (d, $J = 8.3$ Hz, 4H, 18-*o*, 4-CF₃Ph), 6.68 (d, $J = 8.0$ Hz, 4H, 17-*m*, 4-CF₃Ph), 6.68 (b, 12-*o*, 4-CF₃Ph), 6.62 (d, $J = 8.0$ Hz, 4H, 13-*m*, 4-CF₃Ph), 6.40 (d, $J = 7.9$ Hz, 4H, 17-*o*, 4-CF₃Ph), 6.30 (d, $J = 8.0$ Hz, 4H, 13-*o*, 4-CF₃Ph), 6.28 (d, $J = 7.9$ Hz, 4H, 15-*o*, 4-CH₃Ph), 5.86 (d, $J = 7.8$ Hz, 4H, 15-*m*, 4-CH₃Ph), 2.39 (s, 1H, -OH), 1.98 (s, 3H, 10-*p*, 4-CH₃Ph), 1.80 (s, 6H, 5,15-*p*, 4-CH₃Ph). ¹⁹F NMR (CDCl₃): δ -63.06 (s, 6F), -63.15 (s, 6F), -63.19 (s, 6F), -63.54 (s, 6F). MS (HR-ESI, major isotopomer): $[M + H]^+ = 1738.4135$ (expt), 1738.4177 (calcd).

Single-crystal X-ray diffraction analysis of Undecaarylisorcorrole H₂[(CF₃)₈Me₃(5-OH)]. X-ray data for H₂[(CF₃)₈Me₃(5-OH)] were collected on beamline 11.3.1 at the Advanced Light Source, Lawrence Berkeley National Laboratory. Samples were mounted on MiTeGen[®] kapton loops and placed in a 100(2) K nitrogen cold stream provided by an Oxford Cryostream 700 Plus low temperature apparatus on the goniometer head of a Bruker D8 diffractometer equipped with a APEX-II CCD detector. Diffraction data were collected with synchrotron radiation monochromated using silicon(111) to a wavelength of 0.7749(1) Å. An approximate full-sphere of data was collected using a ω scans with scan rates of 3 seconds per 0.5 degree with $2\theta = -36^\circ$. The structures were solved by intrinsic phasing (SHELXT) and refined by full-matrix least squares on F^2 (SHELXL-2014). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were geometrically calculated and refined as riding atoms. The hydrogen atoms on the nitrogen and oxygen atoms were found in the Fourier difference map and allowed to ride on their respective N or O atoms. Additional crystallographic information has been summarized in Table

1 and full details can be found in the crystallographic information file provided in the Supplementary Information.

Undecaarylisorcorrole $\text{H}_2[\text{H}_8\text{Me}_3(5\text{-OH})]$. Into a 50 mL round-bottomed flask, 12 mg (0.0097 mmol) of $\text{Cu}[\text{H}_8\text{Me}_3]$ was added and dissolved in 2 mL of CH_2Cl_2 . Subsequently, 2 mL of concentrated H_2SO_4 (95-97%, Merck) was added. The mixture was stirred and sonicated at room temperature. The progress of the reaction was monitored by ESI mass spectrometry. After 2 hours the reaction was quenched by pouring the mixture into 300 mL distilled H_2O and then extracted with CHCl_3 . The brown organic phase was washed once with distilled water and once with saturated aqueous NaHCO_3 . Upon washing with NaHCO_3 the color of organic phase changed from brown to green. The organic phase was dried with anhydrous Na_2SO_4 , filtered and evaporated under vacuum. The residue obtained was chromatographed on a silica gel column with $\text{CH}_2\text{Cl}_2/5\%\text{-MeOH}$. The product was further purified by PLC with 1:2 *n*-hexane/ CH_2Cl_2 . The olive-green band at the bottom of the plate was pure $\text{H}_2[\text{H}_8\text{Me}_3(5\text{-OH})]$. Yield: 5.6 mg, 48%. UV-vis (CH_2Cl_2): λ_{max} , nm ($\epsilon \times 10^{-4}$, $\text{M}^{-1} \text{cm}^{-1}$): 439 (0.69), 689 (0.15). ^1H NMR (C_6D_6 , 600 MHz, δ in ppm): δ 8.22 (d, $J = 7.8$ Hz, 2H, 5-*o*, 4- CH_3Ph), 7.07 (d, $J = 7.2$ Hz, 2H, 3-*o*, Ph), 7.04 (d, $J = 8.1$ Hz, 2H, 5-*m*, 4- CH_3Ph), 7.03 (o, 7-*o*, Ph), 7.0 (b, 1H, 10-*o*, 4- CH_3Ph), 6.94 (d, $J = 7.2$ Hz, 2H, 2-*o*, Ph), 6.94 (o, 7-*p*, Ph), 6.86 (t, $J = 7.5$ Hz, 2H, 3-*m*, Ph), 6.81 (d, $J = 7.2$ Hz, 1H, 3-*p*, Ph), 6.77 (o, 7-*m*, Ph), 6.73 (o, 7-*m*, Ph), 6.66 (o, 7-*o*, Ph), 6.56 (t, $J = 6.8$ Hz, 2H, 2-*m*, Ph), 6.56 (o, 15-*o*, 4- CH_3Ph), 6.55 (o, 8-*m*, Ph), 6.51 (12-*m*, Ph), 6.48 (o, 15-*m*, 4- CH_3Ph), 6.43 (o, 8-*m*, Ph), 6.37 (b, 1H, 10-*m*, 4- CH_3Ph), 6.23 (b, 1H, 10-*o*, 4- CH_3Ph), 5.56 (b, 1H, 10-*m*, 4- CH_3Ph), 2.52 (s, 1H, -OH), 2.08 (s, 3H, 5-*p*, 4- CH_3Ph), 1.82 (s, 3H, 15-*p*, 4- CH_3Ph), 1.68 (s, 3H, 10-*p*, 4- CH_3Ph). MS (HR-ESI major isotopomer): $[\text{M} + \text{H}]^+ = 1193.5179$ (expt), 1193.5153 (calcd).

Undecaarylisorcorrole $\text{H}_2[(\text{CF}_3)_8\text{H}_3(5\text{-OH})]$. To a solution of $\text{Cu}[(\text{CF}_3)_8\text{H}_3]$ (25 mg, 0.014 mmol) in CH_2Cl_2 (7.0 mL) was added dropwise 1 mL H_2SO_4 (95-97%) and the resulting suspension was stirred for 30 min. The mixture was poured into cold, distilled water and extracted with CH_2Cl_2 . The green organic phase was washed once with distilled H_2O and once with saturated aqueous NaHCO_3 , dried with anhydrous Na_2SO_4 , and filtered. After concentration to a minimum volume, the organic phase was chromatographed on a silica gel column with 1:1 hexane/ CH_2Cl_2 , whereupon the isocorrole isomers eluted as a green band. PLC with 3:2 hexane/ CH_2Cl_2 yielded the 5-OH-isocorrole (17mg, 0.01, 71.6%) as the first intense green band. Free base $\text{H}_3[(\text{CF}_3)_8\text{H}_3]$ (1.8 mg, 7%) followed as a second, thinner green band, closely followed by a third, bright green band containing the 10-OH-isocorrole (2.5 mg, 11%). The latter two

products were not fully characterized because of the small quantities obtained so analytical data are only reported for the 5-OH isomer. UV-Vis (CH₂Cl₂): λ_{max} , nm ($\epsilon \times 10^{-4}$, M⁻¹cm⁻¹): 433 (4.30), 681 (0.98). ¹H NMR (C₆D₆): δ 8.0 (d, 2H, 5-*o*, Ph), 7.20 (m, 1H, 7-*m*, 4-CF₃Ph), 7.15 (t, 2H, 5-*m*, Ph); 7.05 - 7.0 (m, 3H, 5-*p*, Ph and 3-*m*, 4-CF₃Ph), 6.82 (d, 2H, 3-*o*, 4-CF₃Ph), 6.75 (d, 1H, 10-*o*, Ph), 6.75- 6.56 {m, 7-*m* (1H, 4-CF₃Ph), 2-*o*, *m* (4H, 4-CF₃Ph), 8-*m* (1H, 4-CF₃Ph), 7-*o* (1H, 4-CF₃Ph), 15-*m* (2H, Ph)}, 6.54 (d, 1H, 8-*m*, 4-CF₃Ph), 6.42 (d, 1H, 7-*o*, 4-CF₃Ph), 6.40 – 6.25 {m, 15-*p* (1H, Ph), 10-*m* (1H, Ph), 8-*o* (2H, 4-CF₃Ph), 15-*o* (2H, Ph)}, 6.20 (t, 1H, 10-*p*, Ph), 6.10 (d, 1H, 8-*o*, 4-CF₃Ph), 6.0 (d, 1H, 10-*o*, Ph), 5.65 (t, 1H, 10-*m*, Ph). ¹⁹F NMR (C₆D₆)₂: δ -62.88 (s, 3F), -63.02 (s, 3F), -63.41 to -63.46 (m, 3F), -63.48 (s, 6F), -63.53 (s, 3F), -63.61 (s, 3F), -63.71 to -63.76 (m, 3F). HRMS (ESI⁺, major isotopomer): [M + H]⁺ = 1696.3692 (expt), 1696.3708 (calcd). Elemental analysis. Found (calcd) : C, 65.86 (65.88); H, 3.20 (2.97), N, 3.27 (3.30).

Synthesis of gold β -octakis(*p*-trifluoromethylphenyl)-*meso*-triphenylcorrole,

Au[(CF₃)₈H₃]. Gold(III) acetate (11 mg, 5 equiv) was added to a green solution of a mixture of the isomeric isocorroles H₂[(CF₃)₈H₃(5/10-OH)] (15 mg, 0.009 mmol) pyridine (5.0 mL). After overnight stirring, the resulting reddish-brown suspension was evaporated and the residue eluted through silica gel with 7:3 hexane/CH₂Cl₂, yielding the gold undecaarylcorrole as the first red band (7 mg, 41.5%). Vapour diffusion of hexane into a CH₂Cl₂ solution yielded tiny rectangular needles of x-ray quality in approximately a month. UV-Vis (CH₂Cl₂): λ_{max} , nm ($\epsilon \times 10^{-4}$, M⁻¹cm⁻¹): 434 (6.08), 544 (0.58). 580 (2.0). ¹H NMR (600 MHz, (CDCl₃)₂): δ 7.29 (d, *J* = 8.2 Hz, 4H, 2,18-*o*, 4-CF₃Ph), 7.15 (d, 4H, 5, 15-*o*, Ph), 7.09 (d, 2H, 10-*o*, Ph), 7.05 (d, *J* = 8.1 Hz, 4H, 3,17-*o*, 4-CF₃Ph), 7.02 (d, *J* = 8.1 Hz, 4H, 2,18-*m*, 4-CF₃Ph), 6.96 (d, *J* = 7.9 Hz, 4H, 3,17-*m*, 4-CF₃Ph), 6.93 – 6.89 (m, 8H, 7, 8, 12,13-*m*, 4-CF₃Ph), 6.87 (d, *J* = 8.0 Hz, 4H, 7,13-*o*, 4-CF₃Ph), 6.82 (d, *J* = 7.9 Hz, 4H, 8,12-*o*, 4-CF₃Ph), 6.74 (t, *J* = 7.7 Hz, 2H, 5,15-*p*, Ph), 6.65 (t, *J* = 7.6 Hz, 1H, 10-*p*, Ph), 6.49 (t, *J* = 7.7 Hz, 4H, 5,15-*m*, Ph), 6.41 (t, *J* = 7.7 Hz, 2H, 10-*m*, Ph). ¹⁹F NMR (CDCl₃): δ -63.31 (s, 12F); -63.42 (s, 6F); -63.49 (s, 6F). HRMS (ESI⁺, major isotopomer): [M]⁺ = 1873.3112 (expt), 1873.3110 (calcd). Elemental analysis. Found (calcd) : C, 59.90 (59.63); H, 2.77 (2.53), N, 3.11 (2.99).

Single-crystal X-ray diffraction analysis of the gold undecaarylcorrole Au[(CF₃)₈H₃].

X-ray data for Au[(CF₃)₈H₃] were collected on beamline 11.3.1 at the Advanced Light Source, Lawrence Berkeley National Laboratory. A red tablet with dimensions 50 x 40 x 15 μm^3 was mounted on a MiTeGen[®] kapton loop and placed in a 100(2) K nitrogen cold stream provided by an Oxford Cryostream 700 Plus low temperature apparatus on the goniometer head of a Bruker

D8 diffractometer equipped with a PHOTON100 CMOS detector operating in shutterless mode. Diffraction data were collected with synchrotron radiation monochromated using silicon(111) to a wavelength of 0.7749(1) Å. An approximate full-sphere of data was collected using a combination of ϕ and ω scans with scan speeds of 1 second per degree for the ϕ scans, and 1 and 3 seconds per degree for the ω scans at $2\theta = 0$ and -45° , respectively. The structures were solved by intrinsic phasing (SHELXT) and refined by full-matrix least squares on F^2 (SHELXL-2014). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were geometrically calculated and refined as riding atoms. Additional crystallographic information has been summarized in Table 1 and full details can be found in the crystallographic information file provided in the Supporting Information.

Supporting information. UV-vis, ^1H NMR, and high-resolution mass spectra (42 pages); crystallographic information files for $\text{H}_2[(\text{CF}_3)_8\text{Me}_3(5\text{-OH})]$ and $\text{Au}[(\text{CF}_3)_8\text{H}_3]$.

Acknowledgement. This work was supported by the of the Research Council of Norway (FRINATEK project 231086, AG) and the Advanced Light Source, Berkeley, California (CMB, KJG). The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

References

-
- [1] For a review on applications of corroles, see: I. Aviv-Harel, Z. Gross, *Chem. Eur. J.* 15 (2009) 8382–8394.
 - [2] K. E. Thomas, A. B. Alemayehu, J. Conradie, C. M. Beavers, A. Ghosh, *Acc. Chem. Res.* 45 (2012) 1203–1214.
 - [3] J. H. Palmer, *Struct. Bond.* 142 (2012) 49–89.
 - [4] H. L. Buckley, J. Arnold, *Dalton Trans.* 44 (2015) 30–36.
 - [5] C. Capar, K. E. Thomas, A. Ghosh, *J. Por. Phthalocya.* 12 (2008) 964–967.
 - [6] F. Mandoj, S. Nardis, G. Pomarico, R. Paolesse, *J. Por. Phthalocya.* 12 (2008) 19–26.
 - [7] H. Y. Liu, L. Chen, F. Yam, H. Y. Zhan, X. Ying, X. L. Wang, H. F. Jiang, C. K. Chang, *Chin. Chem. Lett.* 19 (2008) 1000–1003.
 - [8] T. H. Ngo, W. Van Rossom, W. Dehaen, W. Maes, *Org. Biomol. Chem.* 7 (2009) 439–443.
 - [9] C. Capar, L.-K. Hansen, J. Conradie, A. Ghosh, *J. Por. Phthalocya.* 14 (2010) 509–512.

-
- [10] J. Capar, J. Conradie, C. M. Beavers, A. Ghosh, *J. Phys. Chem. A* 119 (2015) 3452–3457.
- [11] J. Capar, S. Berg, K. E. Thomas, C. M. Beavers, K. J. Gagnon, A. Ghosh, *J. Inorg. Biochem.* 153 (2015) 162–166.
- [12] A. Alemayehu, A. Ghosh, *J. Por. Phthalocya.* 15 (2011) 106–110.
- [13] E. Rabinovitch, I. Goldberg, Z. Gross, *Chem. Eur. J.* 17 (2011) 12294–12301.
- [14] A. M. Albrett, K. E. Thomas, S. Maslek, A. Młodzianowska, J. Conradie, C. M. Beavers, A. Ghosh, P. J. Brothers, *Inorg. Chem.* 53 (2014) 5486–5493.
- [15] S. Berg, K. E. Thomas, C. M. Beavers, A. Ghosh, *Inorg. Chem.* 51, (2012) 9911–9916.
- [16] D. Gao, G. Canard, M. Giorgi, T. S. Balaban, *Eur. J. Inorg. Chem.* (2012) 5915–5920.
- [17] D. Gao, G. Canard, M. Giorgi, P. Vanloot, T. S. Balaban, *Eur. J. Inorg. Chem.* (2013) 279–287.
- [18] J. I. Setsune, A. Tsukajima, J. Watanabe, *Tetrahedron Lett.* 47 (2006) 1817–1820.
- [19] G. Pomarico, X. Xiao, S. Nardis, R. Paolesse, F. R. Fronczek, K. M. Smith, Y. Fang, Z. Ou, K. M. Kadish, *Inorg. Chem.* 49 (2010) 5766–5774.
- [20] D. L. Flint, R. L. Fowler, T. D. LeSaulnier, A. C. Long, A. Y. O’Brien, G. R. Geier, *J. Org. Chem.* 75 (2010) 553–563.
- [21] R. Costa, G. R. Geier, C. J. Ziegler, *Dalton Trans.* 40 (2011) 4384–4386.
- [22] S. Nardis, G. Pomarico, F. R. Fronczek, M. G. H. Vicente, R. Paolesse, *Tetrahedron Lett.* 48 (2007) 8643–8646.
- [23] D. Sakow, D. Baabe, B. Böker, O. Burghaus, M. Funk, C. Kleeberg, D. Menzel, C. Pietzonka, M. Bröring, *Chem. Eur. J.* 20 (2014) 2913–2924.
- [24] M. Ethirajan, Y. Chen, P. Joshi, R. K. Pandey, *Chem. Soc. Rev.* 40 (2011) 340–362.
- [25] M. Stefanelli, J. Shen, W. Zhu, M. Mastroianni, F. Mandoj, S. Nardis, Z. Ou, K. M. Kadish, F. R. Fronczek, K. M. Smith, R. Paolesse, *Inorg. Chem.* 48 (2009) 6879–6887.
- [26] P. Świder, A. Nowak-Król, R. Voloshchuk, J. P. Lewtak, D. T. Gryko, W. Danikiewicz, *J. Mass Spectrom.* 45 (2010) 1443–1451.
- [27] J. Wojaczyński, M. Duszak, L. Latos-Grazyński, *Tetrahedron* 69 (2013) 10445–10449.
- [28] C. Tardieux, C. P. Gros, R. Guillard, *J. Heterocycl. Chem.* 35 (1998) 965–970.
- [29] G. R. Geier, J. F. B. Chick, J. B. Callinan, C. G. Reid, W. P. Auguscinski, *J. Org. Chem.* 69 (2004) 4159–4169.

-
- [30] For an extensive study of free-base corrole conformation, see: J. Capar, J. Conradie, C. M. Beavers, A. Ghosh, *J. Phys. Chem. A* 119 (2015) 3452–3457.
- [31] C. J. Ziegler, J. R. Sabin, G. R. Geier, V. N. Nemykin, *Chem. Comm.* 48 (2012) 4743–4745.
- [32] K. E. Thomas, A. B. Alemayehu, J. Conradie, C. M. Beavers, A. Ghosh, *Inorg. Chem.* 50 (2011) 12844–12851.
- [33] K. E. Thomas, C. M. Beavers, A. Ghosh, *Mol. Phys.* 110 (2012) 2439–2444.
- [34] Auophilic interactions of approximately 4.93–4.35 Å have been observed in a crystal structure of a gold triarylcorrole.^[Error! Bookmark not defined.a]
- [35] A. B. Alemayehu, L.-K. Hansen, A. Ghosh, *Inorg. Chem.* 49 (2010) 7608–7610.
- [36] K. E. Thomas, H. Vazquez-Lima, Y. Fang, Y. Song, K. J. Gagnon, C. M. Beavers, K. M. Kadish, A. Ghosh, *Chem. Eur. J.* 21 (2015) 16839–16847.
- [37] I. H. Wasbotten, T. Wondimagegn, A. Ghosh, *J. Am. Chem. Soc.* 124 (2002) 8104–8116.

For Table of Contents only:

Synopsis: Free-base undecaarylisoctrololes are presented as a new class of sterically hindered macrocyclic ligands. One of these has been complexed, with concomitant aromatization, to yield a gold(III) undecaarylcorrole. Both a free-base undecaarylisoctrolole and the gold undecaarylcorrole were fully structurally characterized. The significant solubility of the gold complex appears to be related to the absence of aurophilic/metallophilic interactions.

Table 1

Table 1. Crystallographic data for $\text{H}_2[(\text{CF}_3)_8\text{Me}_3(5\text{-OH})]$.

Sample	$\text{H}_2[(\text{CF}_3)_8\text{Me}_3(5\text{-OH})]$	$\text{Au}[(\text{CF}_3)_8\text{H}_3]$
Chemical formula	$\text{C}_{96}\text{H}_{56}\text{F}_{24}\text{N}_4$	$\text{C}_{95}\text{H}_{51}\text{F}_{24}\text{N}_4\text{Cl}_4\text{Au}$
Formula mass	1737.44	2043.16
Crystal system	Triclinic	Triclinic
Space group	$P\ 1$	$P\ -1$
$\lambda\ (\text{\AA})$	0.7749	0.7749
$a\ (\text{\AA})$	12.783(3)	15.4998(6)
$b\ (\text{\AA})$	18.085(4)	16.8410(6)
$c\ (\text{\AA})$	18.600(4)	16.9639(6)
$\alpha\ (\text{deg.})$	102.363(3)	106.229(2)
$\beta\ (\text{deg.})$	108.203(3)	91.961(2)
$\gamma\ (\text{deg.})$	96.468(3)	106.901(2)
Z	2	2
$V\ (\text{\AA}^3)$	3914.7(15)	4035.8(3)
Temperature (K)	100(2)	100(2)
Density (g/cm^3)	1.474	1.681
Measured reflections	40303	78866
Unique reflections	15237	29236
Parameters	1169	1256
Restraints	66	646
R_{int}	0.0670	0.0524
θ range (deg.)	2.587 – 28.553	2.165 – 36.007
R_1, wR_2 all data	0.0683, 0.2226	0.0459, 0.1140
S (GooF) all data	1.024	1.030
Max/min res. Dens. ($\text{e}/\text{\AA}^3$)	0.410/-0.349	2.151/-1.956

Figure 1

*same charge/
proticity*

similar sterics

Figure 2

Figure 3

$M[Y_8X_3]$

$H_2[Y_8X_3(5-OH)]$

$H_2[Y_8X_3(10-OH)]$

Figure 4

Figure 5

Figure 6

Figure 7

(a)

(b)

For Table of Contents only:

Synopsis: Free-base undecaarylisorroles are presented as a new class of sterically hindered macrocyclic ligands. One of these has been complexed, with concomitant aromatization, to yield a gold(III) undecaarylcorrole. Both a free-base undecaarylisorrole and the gold undecaarylcorrole were fully structurally characterized. The significant solubility of the gold complex appears to be related to the absence of aurophilic/metallophilic interactions.