# Gold(I) and Gold(III) Corroles

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12294 -

Abstract: Corrole complexes with gold(I) and gold(III) were synthesized and their structural, photophysical, and electrochemical properties investigated. This work includes the X-ray crystallography characterization of gold(I) and gold(III) complexes, both chelated by a corrole with fully brominated  $\beta$ -pyrrole carbon atoms. The mononuclear and chiral gold(I) corrole appears to be the first of its kind within the porphyrinoid family, while the most unique property of the gold(III) corrole is that it displays phosphorescence at ambient temperatures.

## Introduction

The use of gold complexes in catalysis is constantly increasing,<sup>[1]</sup> mainly by taking advantage of their carbophilic Lewis acidity for the activation of carbon–carbon  $\pi$  bonds. Reviews on the broad array of gold-catalyzed reactions reveal that the majority of homogeneous catalysts used to date are gold(III) halides or cationic [Au(PPh<sub>3</sub>)]<sup>+</sup> fragments.<sup>[2,3]</sup> Divalent gold complexes are much more rare and mostly restricted to complexes with unsaturated dithiolate and porphyrin ligands,<sup>[4,5]</sup> where delocalization of the unpaired electron through the  $\pi$  system is possible.<sup>[6]</sup> The most prominent research direction on gold(III) porphyrins appears to be their utilization as anticancer drugs, with indications that they may be of larger potency than *cis*-platin.<sup>[7]</sup> Since gold-(III) porphyrins may easily be reduced by either metal- or ligand-centered processes, they are also used as acceptors in photosynthesis-mimicking dyads<sup>[8,9]</sup> and triads.<sup>[10,11]</sup> There is only a singular report about the catalytic properties of gold-(III) porphyrins (for cycloisomerization of allenones),<sup>[12]</sup> which display higher chemoselectivity than other homogeneous gold(III) catalysts.<sup>[13]</sup> Photophysical properties are also of interest, albeit the emission of gold(III) porphyrins is normally only recordable in frozen glass. One exception is the complex with a modified (N confused) porphyrin: it emits at ambient temperatures, a very rare feature for any gold(III) complex.<sup>[14]</sup>

We have lately become interested in corrole complexes with 5d metals for exploring unique photophysical and catalytic properties that they may display, not at least because of the importance for the pharmaceutical and bioimaging applications that are currently at the forefront of research on the "less heavy" metallocorroles.<sup>[15]</sup> The recently reported bis-amine-coordinated iridium(III) corroles fulfilled the first

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expectations by displaying phosphorescence even at ambient temperature, but these coordinatively saturated complexes cannot be utilized as catalysts due to their substitution inertness.<sup>[16]</sup> We have hence decided to attempt the preparation of gold(III) corroles, which based on the knowledge about copper and silver corroles,<sup>[17–19]</sup> may be expected to form quite stable d<sup>8</sup> square planar and relatively "innocent" complexes (i.e., not containing oxidized ligands). Another focus was on determining the two other plausible oxidation states that may be obtained: gold(I) and gold(II).

### **Results and Discussion**

Based on the experience regarding the insertion of rhodium and iridium into tris-pentafluorophenyl corrole, H<sub>3</sub>-(tpfc).<sup>[16,20,21]</sup> it seemed best to use a gold(I) auration agent. despite the fact that due to the softness of gold(I) it is generally assumed that it will not effectively coordinate to nitrogen atoms.<sup>[22]</sup> Gold(I) complexes with N-donor ligands are indeed much less common than those with P-donor ligands, but the affinity for nitrogen can be increased if one phosphine ligand is present because of the efficient  $\pi$ -acceptor nature of the latter.<sup>[23]</sup> The choice of [MeAu(PPh<sub>3</sub>)] and [ClAu(PPh<sub>3</sub>)] as the metal source revealed that both did react with the pyrrole-brominated corrole  $H_3(Br_8tpfc)$  (1; Scheme 1). The auration occurred under very mild conditions, that is, in a toluene solution for 20 min at room temperature with almost quantitative yield of the isolated product. There was no reaction when THF or chloroform were used as solvents and, surprisingly and for yet undetermined reasons, the non-brominated corrole H<sub>3</sub>(tpfc) could not be aurated by any of the applied reaction conditions.

Similar to N-alkylation and rhodium(I) metalation of corroles,<sup>[24]</sup> the auration of **1** afforded two isomers (**2a** and **2b**, with the latter as the major product), as deduced by NMR spectroscopy. Room temperature spectra were very broad due a variety of dynamic processes, but the resonances recorded at low temperature were sharp and informative. Two sets of NH resonance for each isomer are clearly seen in Figure 1a: at -0.39 ppm and -3.37 ppm for **2b** and at 0.67 ppm and -3.93 ppm for **2a**. Resonances attributable to coordinated PPh<sub>3</sub> are located at relatively high field (6.66 ppm, 6.53 ppm and 5.18 ppm for the major isomer), due to the diamagnetic ring current effect of the aromatic macrocycle. The low temperature <sup>19</sup>F NMR spectra (Fig-

Chem. Eur. J. 2011, 17, 12294-12301



Scheme 1. Synthesis of [(tpfcBr<sub>8</sub>)Au<sup>I</sup>(PPh<sub>3</sub>)], obtained as a mixture of the N22 (2a) and N21 (2b) isomers.

ure 1 b) were even more revealing. The *ortho*-F atoms of the main isomer **2b** are easily identified by the six major resonances at around -135 ppm (accompanied by a similar set for the minor isomer **2a**), which proves that there is no plane of symmetry in these complexes. The such obtained information is fully consistent with the structures drawn in Scheme 1, that is, the products have been assigned as (triphenylphosphine)gold(I) complexes coordinated to monoanionic N21 and N22 corroles (note that two other N atoms remains protonated). Confirmation of the above conclusion, as well as confident assignment of the major isomer **2a** as the N22 coordinated isomer, was obtained via X-ray crystallography performed on green-plate-like crystals obtained from a benzene/heptanes solution (see below).

A EUROPEAN JOURNAL

In contrast with analogous rhodium(I) corroles,<sup>[25]</sup> there was no spontaneous oxidation of 2a/2b to the trivalent complex in aerobic solution. The first attempt to obtain the corresponding gold(III) corrole was by treating a  $[D_6]$ benzene solution of [(tpfcBr<sub>8</sub>)Au<sup>I</sup>(PPh<sub>3</sub>)] with Br<sub>2</sub>, in situ in a NMR tube (Scheme 2). There was an immediate change in color from green to red, no evidence for coordinated triphenylphosphine in the <sup>1</sup>H NMR spectrum, and the <sup>19</sup>F NMR spectrum changed from very complicated to very simple (Figure 2). The 2:1 ratio of the ortho-F, para-F, and meta-F resonances clearly pointed towards the presence of a  $C_2$ symmetry axis, consistent with expectation for the gold(III) corrole 3 (Scheme 2). However, only a minute amount of the above mentioned product was obtained when the reaction was carried out in (non-deuterated) toluene. Instead, the two main products isolated after column chromatography were **4a** and **4b** (in 25% and 30% yield, respectively), identified as N21 and N22 benzyl-tpfcBr<sub>8</sub>, respectively, by NMR (Figure 3). The <sup>19</sup>F NMR spectra served to indicate that the symmetry remained as low as in the reactants, while the high field <sup>1</sup>H resonances were safely assigned to N-ben-



Figure 1. <sup>1</sup>H NMR and <sup>19</sup>F NMR spectra of  $[(tpfcBr_8)Au^{I}(PPh_3)]$  in  $[D_8]$ toluene at 253 K.

zylic protons based on the previously reported N-benzyl derivatives of the non-brominated corrole.<sup>[26]</sup> Both compounds could be recrystallized from benzene/heptanes solution and crystals of the N22 isomer provided good diffraction as to allow for X-ray analysis and conformation of the proposed structure (see below). No such products were obtained



Scheme 2. Reaction products obtained in the reactions of [(tpfcBr<sub>8</sub>)Au<sup>l</sup>(PPh<sub>3</sub>)] (the mixture of **2b** and **2a**) with either Br<sub>2</sub>/toluene or NIS/toluene.

12296 -

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# -137 -138 -139 -150 -151 -162 -163 ppm

Figure 2.  $^{19}F$  NMR spectrum of the gold(III) corrole 3 in [D<sub>6</sub>]benzene at 298 K.



Figure 3. a)  ${}^{1}$ H NMR and b)  ${}^{19}$ F NMR spectra of N21 (**4a**) and N22 (**4b**) benzyl-substituted corroles, respectively, in CDCl<sub>3</sub> at 298 K.

when *N*-bromosuccinimide (NBS) or *N*-iodosuccinimide (NIS) rather than  $Br_2$  were used. The optimal oxidizing agent for converting [(tpfcBr<sub>8</sub>)Au<sup>I</sup>(PPh<sub>3</sub>)] to Au<sup>III</sup>(tpfcBr<sub>8</sub>) was found to be NIS, leading to **3** in an almost quantitative yield. Alternatively, **3** could be obtained directly from **1** via treatment with [ClAu(tht)] (tht=tetrahydrothiophene, Scheme 3), a reagent reported for synthesis of gold(III) porphyrins.<sup>[27]</sup> Recrystallization of the gold(III) corrole from CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:2) or benzene/heptanes (1:2) solutions provided red-plate-like X-ray quality crystals, which allowed



Scheme 3. Synthesis of  $(tpfcBr_8)Au^{III}$  (3), directly from the free base 1.

for its structural elucidation. Complex **3** is stable in the solid state and in anaerobic solutions for extended times, but much less so in aerobic solutions and temperatures higher than 40 °C.

FULL PAPER

On top of allowing for structural verification of the new compounds, the three crystal structures obtained in this study (Figure 4, Figure 5, Figure 6) provide a unique oppor-



Figure 4. ORTEP representation of the saddled N22-benzyl corrole **4b**. Ellipsoids are drawn at the 50% level of probability and H atoms are omitted for clarity. a) Side view. b) Top view, with pentafluorophenyl rings omitted for clarity. Selected bond length [Å] and angles [°]: C43–N22 1.49(1), N22-C43-C44 113.4(9). Deviations from the plane defined by the three non-substituted pyrrole nitrogen atoms [Å]: N22: -0.38; C43: -1.73. Torsion angles between the pyrrole rings: 36, 33.8, 11.2 and 15° for N21–N22, N22–N23, N23–N24, and N24–N21, respectively. Selected bond length [Å] and angles [°] for **5b**: C38–N22 1.483(3), N22-C38-C39 115.3(1). Deviations from the plane of the three non-substituted pyrrole nitrogen atoms [Å]: N22: -0.43; C38: -1.78. Torsion angles between the pyrrole rings: addited pyrrole nitrogen atoms [Å]: N22: -0.43; C38: -1.78. Torsion angles between the pyrrole nitrogen atoms [Å]: N22: -0.43; C38: -1.78. Torsion angles between the pyrrole nitrogen atoms [Å]: N22: -0.43; N23–N24, and N24–N21, respectively.

tunity of gaining significant insight into several interesting aspects of the fully brominated corrole macrocycle. In contrast with the low resolution (large R factor) structure of the pyrrole-brominated corrole  $H_3(Br_8tpfc)$  (1),<sup>[28]</sup> the structure of the N22-benzyl derivative 4b is of good quality (Figure 4, R factor of 0.07) and enables a meaningful comparison with the previously published analogue of the corresponding non-brominated corrole, N22-benzyl-tpfc (5b).<sup>[25]</sup> The corrole macrocycle of 4b deviates severely from planarity predominantly due to the steric hindrance introduced by the N22-benzyl arm. The deviation of the N22 atom from the plane of the three non-substituted pyrrole nitrogen atoms is however only 0.38 Å for 4b, much less than the 0.43 Å in 5b. The same trend is seen for the deviation of the methylene group and its two protons: these atoms are closer to the corrole ring in 4b than in 5b. These observations may be explained by the core size of the corrole macrocycle, as reflected by the distances between the diagonally opposite nitrogen atoms, N21…N23 and N22…N24. The corresponding separations are systematically larger in the brominated derivative **4b** (3.998 Å and 3.861 Å), than in the non-brominated one **5b** (3.993 Å and 3.846 Å). The electronegative withdrawing bromines apparently increase the corrole core size and thus enable a closer approach of the N-benzyl group to

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Figure 5. ORTEP representation of the severely saddled N22 gold(I) complex **2b**. Ellipsoids are drawn at the 50% level of probability and H atoms are omitted for clarity. a) Top view, with phenyl rings omitted for clarity. b) Side view. Selected bond lengths [Å] and angles [°]: Au–N22 2.094(4), Au–P 2.230(1), N22-Au-P 177.3(1). Deviations from the plane of the three non-substituted pyrrole nitrogen atoms [Å]: N22: -0.24; Au: -2.09; P: -4.1. Torsion angles between the pyrrole rings: 26.7, 32.17, 19.4 and 10.9°, for N21–N22, N22–N23, N23–N24, and N24–N21, respectively.



Figure 6. ORTEP representation of the almost perfectly planar (tpfcBr<sub>s</sub>)Au<sup>III</sup>, **3**. Ellipsoids are drawn at the 50% level of probability. Torsion angles between adjacent pyrrole rings: 1.01, 4.29, 2.9 and 1.39° for N21–N22, N22–N23, N23–N24, and N24–N21, respectively. Torsion angle between the macrocycle and the pentafluorophenyl rings: 87.7, 89.78, and 84.85° for the  $C^5$ ,  $C1^0$ , and  $C^{15}$  positions, respectively. Selected bond lengths: 1.93 (2), 1.96 (2), 1.95 (2) and 1.94 (2) Å, for Au–N21, Au–N22, Au–N23, Au–N24, respectively.

the core. These observations are consistent with earlier findings that  $\beta$ -octabromination of *meso*-triarylcorrole derivatives results in expansion of skeletal bond distances of the corrole macrocycle.<sup>[29]</sup> In fact, the smaller core size of the non-brominated corrole may be one of the reasons for its inertness toward the reaction with the gold(I) precursor.

As can be easily seen from Figure 4 and Figure 5, there is no symmetry element in the corrole derivatives that are Nsubstituted by either a benzyl group (**4b**) or by gold(I)triphenylphosphine (**2b**); that is, their symmetry is  $C_1$  and they are chiral. Complex **2b** crystallized in the triclinic  $P\bar{1}$  space group, with two molecules of opposing chirality in an asymmetric unit. The corrole macrocycle is nonplanar and exhibits a saddle-type conformation, with the pyrrole rings around the circle being tilted up and down in an alternating manner. The Au-PPh<sub>3</sub> group is oriented edge-on with respect to the molecular center, and the three pentafluorophenyl groups are oriented roughly perpendicular to the corrole framework. As a result of the large ionic radius of gold(I) (ca. 1.5 Å), the deviations of Au and P atoms from the plane defined by the three non-substituted pyrrole nitrogen atoms is very large (2.09 4.10 Å, respectively, and Figure 4). This may explain the smaller hindrance inside the macrocycle of 2b relative to that in the other N-alkylated derivatives  $(\mathbf{5b}^{[27]} \text{ and } \mathbf{4b})$ , which display much more severe deformation of the corrole core as indicated by the torsion angles between the different pyrrole rings (Figure 4). The X-ray structure of 2b reveals a typical 180° angle between the two ligands of the moiety; P-Au-N22 gold(I)177.3(1)°. The deviation of the N22 atom from the plane of the three nonsubstituted pyrrole nitrogen atoms relatively to other N-alkylated species is small: 0.24 Å for 2b as opposed to 0.43 Å and 0.38 Å for 5b,<sup>[27]</sup> and 4b, respectively. This small deviation can be explained by the long Au-N22 bond (2.094 Å), as compared to other Au-N distances,<sup>[30]</sup> due to a strong trans influence of PPh<sub>3</sub>.

Complex **3** crystallized as heptane solvate in a triclinic  $P\bar{1}$  space group (Figure 6). The small torsion angles between the adjacent pyrrole rings along the ring—1.0, 4.3, 2.9, and

1.4°-serve to illustrate the planarity of the macrocycle in this structure. The pentafluorophenyl residues are practically not twisted from the perpendicular orientation. The Au atom displays only slightly distorted square-planar coordination geometry, with the corresponding Au-N bonds in 3 ranging from 1.93 to 1.98 Å. This may be contrasted with copper corroles (formally in a Cu<sup>III</sup> oxidation state), for which metal( $d_{x^2-y^2}$ )-corrole( $\pi$ -HOMO) orbital interactions were claimed to engender the copper(II) character to the central ion and consequential saddling of the macrocycle.<sup>[18]</sup> In our earlier studies of copper corrole complexes the 23atom corrole macrocycle was found to be significantly ruffled,<sup>[19]</sup> a phenomenon that was later observed by a combination of X-ray crystallography and DFT calculations both in the presence and in the absence of sterically hindered substituents on the corrole periphery.<sup>[18,29]</sup> In structures evaluated experimentally by crystallography the Cu-N(pyrrole) bond length ranges were 1.89-1.90 Å<sup>[18]</sup> and 1.87-1.89 Å,<sup>[19]</sup> considerably shorter than those observed in the gold(III) corrole 3. The lack of evidence for significant core deformation from planarity shared by gold(III), cobalt(III),<sup>[31,32]</sup> and iridium(III) corroles,<sup>[33]</sup> points towards more genuine oxidation states and no strong metal(d)–corrole( $\pi$ ) interaction therein. For low-spin cobalt(III) ions (radius of 0.69 Å is comparable to that of Cu<sup>III</sup>: 0.68 Å) this may be attributed to the difference in the energy levels of the respective d<sub>x<sup>2</sup>-y<sup>2</sup></sub> orbitals. The chemistry of the Ir<sup>III</sup> and Au<sup>III</sup> ions is affected, on the other hand, by the outer f orbitals which shield the delectron shell. The latter two ions also have relatively large ionic radii (0.82 and 0.85 Å, respectively), and their insertion into the corrole favors planar conformation and expanded macrocyclic core. The diagonal N···N distances within the macrocyclic core of **3** are 3.89 and 3.90 Å, thus providing a relaxed square-planar coordination environment for gold-(III), whose ionic radius is about 0.85 Å.

In contrast with the preliminary investigation of Alemayehu and Ghosh,<sup>[34]</sup> the gold corroles obtained in our studies are highly soluble in common organic solvents and their solution properties could hence be confidently investigated. The gold(I) complexes could not be reduced at reasonable potentials, but displayed a semi-reversible redox process with a half wave potential of 1.14 V. Spectroelectrochemical studies revealed that the complex is destroyed upon continuous oxidation at >1.2 V, which rules out electrochemical oxidation as a route to either gold(II) or gold(III) corroles. It is important to add that there is no mononuclear gold(I) complex chelated by any other member of the porphyrinoid family and a comparison could hence not be performed. Cyclic voltammetry of the gold(III) corrole revealed a reversible redox process with a half-wave potential of -0.46 V (Figure 7, inset). Spectroelectrochemical reduction of **3** showed that the Soret band moves from 426 nm to 412 nm (Figure 7) and that the Q bands also move to higher energy, but the reduced species appeared to be not stable enough for a thorough characterization. Nevertheless, we note that the  $E_{1/2}$  for the reduction of **3** is more positive by more than 400 mV than that measured for the analogous gallium(III) corrole (Br<sub>8</sub>tpfc)Ga (it displays an irreversible reduction with an  $I_{pc}$  of -1.29 V), but only by 100 mV relative to the reported gold(III)/gold(II) redox couple reported for a por-



Figure 7. Cyclic voltammetry (inset) and spectroelectrochemistry (at -0.6 V) of (tpfcBr<sub>8</sub>)Au<sup>III</sup> in acetonitrile/0.1 M TBABF<sub>4</sub>.

# **FULL PAPER**

phyrin complex  $(E_{1/2} = -0.56 \text{ V})$ .<sup>[35]</sup> This suggests that the reduction of **3** may involve the metal and not the corrole, but a more a definite assignment of the redox site is not yet possible because of the limited stability of the reduced species.

Preliminary photophysical investigations of the gold(III) corrole **3** revealed that it exhibits phosphorescence at room temperature with an emission maximum at 769 nm (Figure 8). A lifetime of  $(195 \pm 10) \mu$ s and a quantum yield of 0.3% were obtained under a nitrogen atmosphere, while the signal intensity diminished almost completely upon the introduction of air. The room temperature quantum yield and phosphorescence lifetime of **3** appear to be the highest and longest, respectively, reported for any corrole derivative so far.<sup>[36,37]</sup>



Figure 8. Emission spectrum of the gold(III) corrole 3 ( $\lambda_{ex}$ =583 nm) in toluene at 298 K, under a nitrogen atmosphere.

### Conclusion

We have demonstrated the facile auration of corroles to chiral gold(I) corroles, and their clean conversion to gold-(III) corroles, as well as a direct synthetic route to the latter. These new gold complexes, as well as the unexpected byproducts obtained by the reaction of the gold(I) corrole with bromine, were fully characterized by NMR and X-ray crystallography. We have also provided the first report of the chemical, electrochemical, and photophysical properties of gold corroles, including long wavelengths phosphorescence at room temperature. The advantageous utilization of these features in aspects related to energy and human health are currently investigated.

### **Experimental Section**

See the Supporting Information for full experimental details.

Synthesis of the gold(I) corroles, 2a and 2b: A 10 mL toluene solution of 1 (50 mg, 0.035 mmol) was treated with [MeAu(PPh<sub>3</sub>)] (16 mg, 0.035 mmol) or [ClAu(PPh<sub>3</sub>)] at room temperature for 30 min, followed by silica-gel chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/hexanes = 1:10, as eluent) purification. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/pentane (1:10) provided

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- 12299

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*Compound* **2a**: <sup>1</sup>H{<sup>31</sup>P} NMR (600 MHz, [D<sub>8</sub>]toluene, 232 K):  $\delta$ =6.49 (m, 6H), 6.27 (t, *J*=7.65 Hz, 3H), 5.17 (t, *J*=7.65 Hz, 6H), 0.67 (s, 1H), -3.93 ppm (s, 1H); <sup>19</sup>F NMR (565 MHz, [D<sub>8</sub>]toluene, 232 K):  $\delta$ = -132.26 (d, *J*=21.60 Hz, 1F), -132.63 (d, *J*=21.60 Hz, 1F), -133.29 (d, *J*=18.52 Hz, 1F), -133.87 (d, *J*=18.52 Hz, 1F), -134.02 (d, *J*=15.43 Hz, 1F), -135.47 (d, *J*=21.60 Hz, 1F), -146.57 (t, *J*=19.16 Hz, 1F), -146.91 (t, *J*=19.16 Hz, 1F), -147.58 ppm (t, *J*=19.16 Hz); <sup>31</sup>P{<sup>1</sup>H} NMR (243 MHz, [D<sub>8</sub>]toluene, 232 K):  $\delta$ =26.76 ppm; UV/Vis (toluene):  $\lambda_{max}$  ( $\varepsilon \times 10^{-5}$ )=456 (0.92), 606 (0.16), 679 nm (0.13).

*Compound* **2***b*: <sup>1</sup>H[<sup>31</sup>P] NMR (600 MHz, [D<sub>8</sub>]toluene, 232 K):  $\delta$ =6.66 (t, J=7.31 Hz, 3 H), 6.53 (t, J=7.31 Hz, 6 H), 5.18 (d, J=7.22 Hz, 6 H), -0.39 (s, 1 H), -3.37 ppm (s, 1 H); <sup>19</sup>F NMR (565 MHz, [D<sub>8</sub>]toluene, 232 K):  $\delta$ =-131.86 (d, J=21.93 Hz, 1F), -133.17 (d, J=21.93 Hz, 1F), -133.60 (d, J=21.93 Hz, 1F), -133.36 (d, J=21.93 Hz, 1F), -133.36 (d, J=21.93 Hz, 1F), -136.90 (d, J=19.19 Hz, 1F), -146.26 (t, J=19.86 Hz, 1F), -147.16 (t, J=19.86 Hz, 1F), -147.31 (t, J=19.86 Hz, 1F), -158.81 (t, J=18.75 Hz, 1F), -158.64 (t, J=18.75 Hz, 1F), -158.81 (t, J=18.75 Hz, 1F), -159.04 (t, J=18.75 Hz, 1F), -159.47 (t, J=18.75 Hz, 1F), -159.49 ppm (t, J=18.75 Hz, 1F); <sup>31</sup>P[<sup>1</sup>H] NMR (243 MHz, [D<sub>8</sub>]toluene, 232 K):  $\delta$ =28.61 ppm; UV/Vis (toluene):  $\lambda_{max}$  ( $\varepsilon$ ×10<sup>-5</sup>)=456 (0.92), 606 (0.16), 679 nm (0.13).

### Synthesis of the gold(III) corrole 3

Method a) From 2a/2b: A 2 mL toluene solution of NIS (5.6 mg, 0.025 mmol) was added dropwise to a 5 mL toluene solution of 2a/2b (20 mg, 0.01 mmol) and the reaction mixture was stirred at room temperature for 30 min, after which the reaction was quenched by 15 mL of H<sub>2</sub>O. Extraction with CH<sub>2</sub>Cl<sub>2</sub> was followed by addition of hexane and **3** was precipitated at 4°C as a red powder in 95% yield (16 mg).

Method b) Directly from **I**: [ClAu(tht)] (10 mg, 0.03 mmol) was added to a solution of **1** (12 mg, 0.008 mmol) in chloroform (10 mL) containing few drops of pyridine. The solution was stirred at room temperature for 30 min under nitrogen atmosphere. The product was purified by neutral alumina chromatography (hexane as an eluent) with a 88% yield. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/pentane (1:2) or benzene/heptane (1:2) solutions provided red-plate-like crystals. <sup>19</sup>F NMR (376.75 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ = -136.70 (dd,  $J^{I}_{\rm F-F}$ =7.54 Hz,  $J^{2}_{\rm F-F}$ =24.52 Hz, 2F), -137.41 (dd,  $J^{3}_{\rm F-F}$ = 7.78 Hz,  $J^{4}_{\rm F-F}$ =24.33 Hz, 4H), -150.37 (t,  $J^{4}_{\rm F-F}$ =22.46 Hz, 2F), -150.78 (t,  $J^{2}_{\rm F-F}$ =21.33 Hz, 1F), -162.65 (td,  $J^{3}_{\rm F-F}$ =7.41 Hz,  $J^{4}_{\rm F-F}$ =23.58 Hz, 4F), -163.10 (td,  $J^{I}_{\rm F-F}$ =7.41 Hz,  $J^{2}_{\rm F-F}$ =22.23 Hz, 2F); UV/Vis (toluene):  $\lambda_{\rm max}$  ( $\epsilon \times 10^{-5}$ )=428 (1.11), 543 (0.11), 580 nm (0.368); MS (MALDI TOF LD<sup>-</sup>): *m*/z (typical cluster due to multiple Br isotopes): centered at 1620.00.

Synthesis of 4a and 4b:  $[(tpfcBr_8)Au(PPh_3)]$ , 2, was dissolved in toluene and excess of Br<sub>2</sub> was added. The resulting solution was stirred at room temperature till all the starting material was consumed. Monitoring of the reaction was carried with TLC plates (hexanes/CH<sub>2</sub>Cl<sub>2</sub>=1:2). The products, 4a and 4b, were purified by silica-gel chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/hexanes=1:100, as eluent). The product 4b was recrystallized from a benzene/heptane (1:2) solution to give green needle like crystals in 30 % yield.

Compound **4a**: <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 6.56 (t, *J* = 7.49 Hz, 1 H), 6.36 (t, *J* = 7.49 Hz, 2 H), 4.70 (d, *J* = 7.28 Hz, 2 H), -1.94 (d, *J* = 14.08 Hz, 1 H), -2.54 (d, *J* = 14.08 Hz, 1 H); <sup>19</sup>F NMR (376.75 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = -136.93 (dd, *J* = 7.74, 24.38 Hz, 1 F), -137.86 (dd, *J* = 7.52, 24.45 Hz, 1 F), -137.28 (dd, *J* = 7.74, 24.38 Hz, 1 F), -139.98 (dd, *J* = 7.34, 23.61 Hz, 1 F), -140.18 (dd, *J* = 6.29, 23.61 Hz, 1 F), -149.37 (t, *J* = 19.76 Hz, 1 F), -150.65 (t, *J* = 21.28 Hz, 1 F), -150.85 (t, *J* = 21.79 Hz, 1 F), -161.75 (td, *J* = 8.70, *J* = 23.20 Hz, 1 F), -161.91 (td, *J* = 7.73, 23.20 Hz, 1 F), -162.26 (td, *J* = 7.73, 23.20 Hz, 1 F), -162.71 (td, *J* = 7.73, 23.20 Hz, 1 F), -162.87 (td, *J* = 7.73, 23.20 Hz, 1 F); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon \times 10^{-5}$ ) = 446 (0.99), 616 nm (0.34).

Compound **4b**: <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ ):  $\delta = 6.51$  (t, J = 7.48 Hz, 1H), 6.34 (t, J = 7.71 Hz, 2H), 4.40 (d, J = 7.43 Hz, 2H), -3.23 (d, J = 14.92 Hz, 1H), -3.85 (d, J = 14.92 Hz, 1H); <sup>19</sup>F NMR (376.75 MHz,  $C_6D_6$ ):  $\delta =$  -136.99 (dd, J=7.63, 24.28 Hz, 1F), -137.38 (dd, J=7.63, 24.28 Hz, 1F), -137.53 (dd, J=7.35, 23.90 Hz, 1F), -139.00 (dd, J=7.35, 23.90 Hz, 1F), -139.47 (dd, J=6.43, 23.98 Hz, 1F), -140.81 (dd, J=6.52, 23.05 Hz, 1F), -149.36 (t, J=21.12 Hz, 1F), -150.19 (t, J=21.12 Hz, 1F), -150.53 (t, J=21.12 Hz, 1F), -162.17 (td, J=6.76, 21.52 Hz, 2F), -162.40 (td, J= 7.99, 22.75 Hz, 1F), -162.51 (td, J=8.61, 20.29 Hz, 1F), -162.60 (td, J= 7.99, 23.37 Hz, 1F), -162.80 (td, J=7.38, 23.37 Hz, 1F); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon \times 10^{-5}$ )=465 (0.99), 610 (0.14), 700 nm (0.09).

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- [1] A. S. K. Hashmi, Gold Bull. 2004, 37, 51.
- [2] V. Mamane, T. Gress, H. Krause, A. Furstner, J. Am. Chem. Soc. 2004, 126, 8654.
- [3] D. J. Gorin, F. D. Toste, Nature 2007, 446, 395.
- [4] A. P. Koley, S. Purohit, S. Ghosh, L. S. Prasad, P. T. Manoharan, J. Chem. Soc. Dalton Trans. 1988, 2607.
- [5] G. Gencheva, D. Tsekova, G. Gochev, D. Mehandjiev, P. R. Bontchev, *Inorg. Chem. Commun.* 2003, 6, 325.
- [6] Z. Ou, K. M. Kadish, W. E, J. Shao, P. J. Sintic, K. Ohkubo, S. Fukuzumi, M. J. Crossley, *Inorg. Chem.* **2004**, *43*, 2078.
- [7] C.-M. Che, R. W.-Y. Sun, W.-Y. Yu, C.-B. Ko, N. Zhu, H. Sun, *Chem. Commun.* 2003, 1718.
- [8] A. M. Brun, A. Harriman, V. Heitz, J. P. Sauvage, J. Am. Chem. Soc. 1991, 113, 8657.
- [9] K. Kilsa, J. Kajanus, A. N. Macpherson, J. Martensson, B. Albinsson, J. Am. Chem. Soc. 2001, 123, 3069.
- [10] S. Fukuzumi, K. Ohkubo, W. E, Z. Ou, J. Shao, K. M. Kadish, J. A. Hutchison, K. P. Ghiggino, P. J. Sintic, M. J. Crossley, *J. Am. Chem. Soc.* 2003, *125*, 14984.
- [11] I. M. Dixon, J. P. Collin, J. P. Sauvage, F. Barigelletti, L. Flamigni, Angew. Chem. 2000, 112, 1348; Angew. Chem. Int. Ed. 2000, 39, 1292.
- [12] C.-Y. Zhou, P. W. H. Chan, C.-M. Che, Org. Lett. 2006, 8, 325.
- [13] A. Nijamudheen, D. Jose, A. Datta, J. Phys. Chem. C 2011, 115, 2187.
- [14] M. Toganoh, T. Niino, H. Furuta, Chem. Commun. 2008, 4070.
- [15] E. Nyarko, N. Hanada, A. Habib, M. Tabata, *Inorg. Chim. Acta* 2004, 357, 739.
- [16] J. H. Palmer, A. C. Durrell, Z. Gross, J. R. Winkler, H. B. Gray, J. Am. Chem. Soc. 2010, 132, 9230.
- [17] C. Brückner, C. A. Barta, R. P. Brinas, J. A. K. Bauer, *Inorg. Chem.* 2003, 42, 1673.
- [18] A. B. Alemayehu, E. Gonzalez, L. K. Hansen, A. Ghosh, *Inorg. Chem.* 2009, 48, 7794.
- [19] I. Luobeznova, L. Simkhovich, I. Goldberg, Z. Gross, Eur. J. Inorg. Chem. 2004, 1724.
- [20] Z. Gross, N. Galili, L. Simkhovich, Tetrahedron Lett. 1999, 40, 1571.
- [21] L. Simkhovich, N. Galili, I. Saltsman, I. Goldberg, Z. Gross, *Inorg. Chem.* 2000, 39, 2704.
- [22] R. J. Puddephatt, The Chemistry of Gold, Elsevier, Oxford, 1978.
- [23] Gold: Progress in Chemistry, Biochemistry and Technology (Ed.: H. Schmidbaur), Wiley, New York, **1999**; D. V. Partyka, T. J. Robilotto, M. Zeller, A. D. Hunter, T. G. Gray, Proc. Natl. Acad. Sci. U.S.A. **2008**, 105, 14293–14297.
- [24] L. Simkhovich, A. Mahammed, I. Goldberg, Z. Gross, Chem. Eur. J. 2001, 7, 1041.
- [25] L. Simkhovich, P. Iyer, I. Goldberg, Z. Gross, Chem. Eur. J. 2002, 8, 2595.
- [26] Z. Gross, N. Galili, Angew. Chem. 1999, 111, 2536; Angew. Chem. Int. Ed. 1999, 38, 2366.
- [27] J. C. Chambron, V. Heitz, J. P. Sauvage, New J. Chem. 1997, 21, 237.

# **FULL PAPER**

- [28] L. K. H. C. Capar, J.Conradie and A. Ghosh, J. Porphyrins Phthalocyanines 2010, 14, 509.
- [29] I. H. Wasbotten, T. Wondimagegn, A. Ghosh, J. Am. Chem. Soc. 2002, 124, 8104.
- [30] Gold Chemistry: Applications and Future Directions in the Life Sciences (Ed.: F. Mohr), Wiley-VCH, Weinheim, 2009.
- [31] R. Paolesse, S. Nardis, F. Sagone, R. G. Khoury, J. Org. Chem. 2001, 66, 550.
- [32] R. Paolesse, S. Licoccia, G. Bandoli, A. Dolmella, T. Boschi, *Inorg. Chem.* 1994, 33, 1171.
- [33] J. H. Palmer, M. W. Day, A. D. Wilson, L. M. Henling, Z. Gross, H. B. Gray, J. Am. Chem. Soc. 2008, 130, 7786.
- [34] A. B. Alemayehu, A. Ghosh, J. Porphyrins Phthalocyanines 2011, 15, 106.

- [35] K. M. Kadish, W. E, Z. Ou, J. Shao, P. J. Sintic, K. Ohkubo, S. Fukuzumi, M. J. Crossley, *Chem. Commun.* 2002, 356.
- [36] S. Nardis, F. Mandoj, R. Paolesse, F. R. Fronczek, K. M. Smith, L. Prodi, M. Montalti, G. Battistini, *Eur. J. Inorg. Chem.* 2007, 2345.
- [37] J. Vestfrid, M. Botoshansky, J. H. Palmer, A. C. Durrell, H. B. Gray, Z. Gross, J. Am. Chem. Soc. 2011, 133, 12899.

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