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Gold corroles

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ABSTRACT: Although a variety of conditions proved unsuccessful for gold insertion into β-unsubstituted *meso*-triarylcorroles, refluxing free-base β-octabromo-*meso*-triarylcorrole ligands, $H_3[Br_8T(p\text{-X-P})C]$ (X = MeO, *n*-Bu, CH_3, H, and CF_3), with chloroauric acid in dichloromethane containing a small amount of triethylamine for 30 min led to 54–65% yields of the corresponding gold complexes.

KEYWORDS: gold, corrole, octabromocorrole.

INTRODUCTION

New ligands lead to new coordination chemistry. Porphyrins and related ligands amply illustrate this all too familiar truism. Thus, syntheses of heteroporphyrins, *N*-confused porphyrins and carbaporphyrins, subporphyrins, expanded porphyrins, porphyrazines, and corrolazines have all led to much novel coordination chemistry [1]. The chemistry of corroles is among the most impressive in this regard [2]; ever since the development of simple one-pot syntheses by Gross [3], Paolesse [4] and their coworkers, which were subsequently improved by Gryko [5], corrole chemistry has grown by leaps and bounds. Over the last few years, we have worked on a number of aspects of corroles, focusing particularly on the effects of peripheral substituents on electronic [6, 7] and geometric [8, 9] structure. In the course of this work, we recently found that free-base β-octabromo-*meso*-triarylcorrole ligands, long inaccessible in their free-base forms, could be synthesized *via* reductive demetalation of the corresponding copper complexes [10, 11]. We hoped that the new ligands would lead to new coordination complexes that cannot be made from β-unsubstituted corrole ligands. This hope has now been realized with the synthesis of a family of gold(III) complexes with systematically varying *meso*-aryl substituents, as described below.

Corrole researchers have long sought to synthesize gold complexes, without success, and our preliminary experiments afforded insight into the problem. With chloroauric acid ($H_3O^+AuCl_4^-$) as the gold(III) source and the β-unsubstituted *meso*-triarylcorrole ligands $H_3[T(p\text{-X-P})C]$ (X = MeO, CH_3, H, CF_3) and *meso*-tris (pentafluorophenyl-corrole), mass spectrometric analysis of the products indicated intractable mixtures of mono-, di-, tri- and tetra-chlorinated free-base corrole products, as well as small amounts of dimeric corroles, arising presumably from Au(III)-promoted oxidative coupling. We surmised that free-base β-octabromo-*meso*-triarylcorrole ligands, $H_3[Br_8T(p\text{-X-P})C]$, which we have recently developed in our laboratory [10, 11], might lend themselves to effective gold insertion, an insight that ultimately proved correct.

RESULTS AND DISCUSSION

Finding an optimum solvent for gold insertion involved much trial and error. Refluxing pyridine, which is commonly used for metalation of both porphyrins and corroles, proved unsatisfactory; although gold insertion with chloroauric acid was observed after prolonged refluxing (> 14 h), the yields were poor and isolation of the Au corroles was correspondingly difficult. Refluxing toluene, methanol, and DMF, with or without an added base (triethylamine), all failed to result in gold insertion. Refluxing dichloromethane, with a small amount of triethylamine, however, proved both highly effective and convenient, resulting in yields of 54–65%. Using these conditions, we succeeded in inserting the metal into five different $H_3[Br_8T(p\text{-X-P})C]$ ligands (X = MeO, *n*-Bu,

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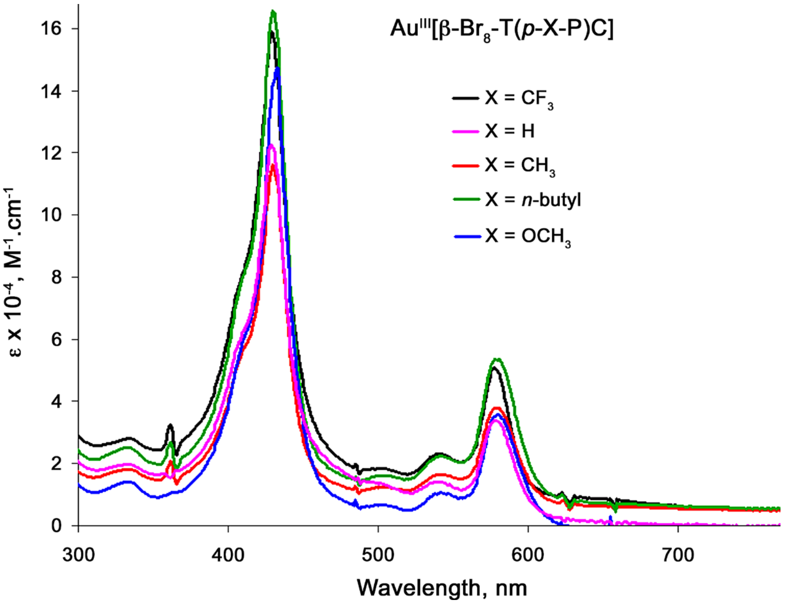

Fig. 1. UV-visible spectra of Au^{III}[Br$_8$T(*p*-X-P)C] in dichloromethane. In each case, the sample concentration was 0.013 ± 0.001 mM

CH$_3$, H, and CF$_3$) [10]. Unambiguous proof of purity and composition of the Au[Br$_8$T(*p*-X-P)C] complexes was obtained from thin-layer chromatography, MALDI-TOF mass spectrometry, ^{1}H NMR spectroscopy and elemental analysis.

Although our primary objective here is to focus on details of the syntheses, certain intriguing properties of gold complexes, relative to the well-studied copper corroles, were immediately obvious. Thus, unlike copper triarylcorroles, whose Soret maxima redshift sensitively in response to electron-donating *para* substituents on the *meso* aryl groups [6, 7], the Soret bands of Au[Br$_8$T(*p*-X-P)C] (Fig. 1) were essentially invariant for X = MeO, *n*-Bu, CH$_3$, H, and CF$_3$. The constancy of the Soret maximum strongly argues for a relative lack of charge transfer character in the gold Soret bands, compared with the analogous copper complexes.

Electrochemical measurements (Fig. 2) support the above argument. As shown in Table 1, the reduction potential of the gold octabromocorroles are lower than those of the analogous copper complexes by over 1.0 V [6, 12], indicating the difficulty of adding an electron to the LUMO, which is substantially metal(d_{x2-y2})-based for all coinage metal corroles. In the same vein, the electrochemical HOMO-LUMO gaps (the difference between $E_{1/2ox}$ and $E_{1/2red}$) of about 2.3 V of the gold complexes are far higher than those of both copper and silver corroles, which are typically around 1.2–1.5 V. The apparent lack of charge transfer character in the gold Soret bands is thus reasonably attributed to a very high-energy metal d_{x2-y2} orbital as well as to a large HOMO-LUMO gap.

When characterizing the Au[Br$_8$T(*p*-X-P)C] derivatives (X = MeO, H, and CF$_3$), an unexpected complication arose, involving the solubility of the compounds; the gold complexes proved considerably less soluble than their copper analogues. Even obtaining ^{1}H NMR spectra proved troublesome or impossible with CDCl$_3$, CD$_2$Cl$_2$, benzene-*d$_6$*, DMSO-*d$_6$*, DMF-*d$_7$*, methanol-*d$_4$*, and acetone-*d$_6$* as solvent. Finding a solvent for electrochemical studies proved similarly troublesome [13]. Fortunately, the complexes are modestly soluble in 1,2-dichlorobenzene, which finally allowed the determination of ^{1}H NMR spectra and cyclic voltammograms. Because the X = CH$_3$ complex was marginally more soluble than the other three, *i.e.* X = MeO, H, and CF$_3$, we decided to synthesize the X = *n*-Bu analogue in the hope of obtaining a much more soluble gold corrole. The *n*-Bu complex did prove more soluble than the others (allowing for example cyclic voltammetry experiments in dichloromethane [14]) but only modestly so. Unfortunately, the involatile character of 1,2-dichlorobenzene, the

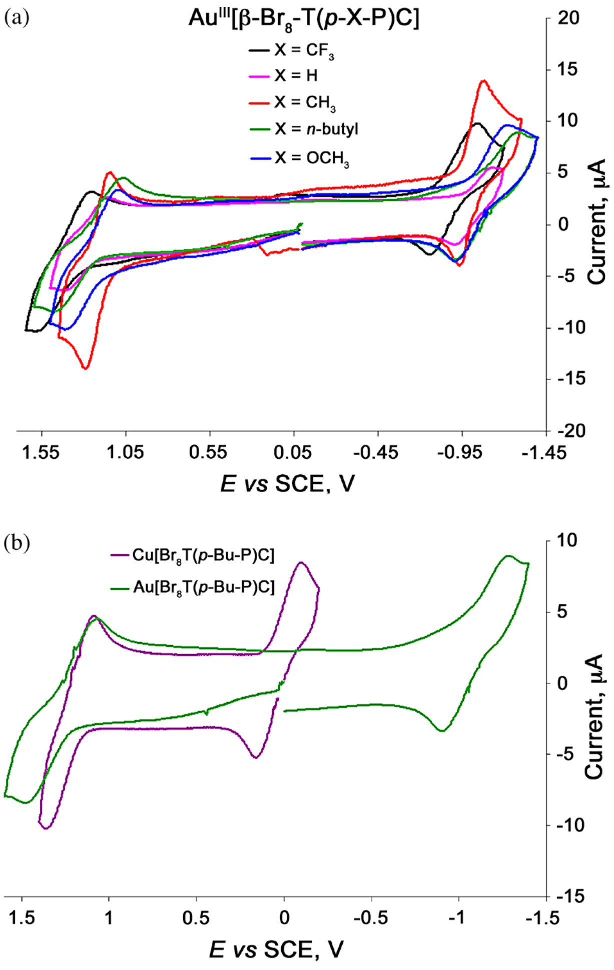

Fig. 2. (a) Cyclic voltammograms of Au[Br$_8$T(*p*-X-P)C] in 1,2-dichlorobenzene; (b) comparison of Cu[Br$_8$T(*p*-Bu-P)C and Au[Br$_8$T(*p*-Bu-P)C]

Table 1. Half-wave potentials ($E_{1/2}$, V *vs.* SCE) for Cu and Ag corroles in CH_2Cl_2 and for Au corroles in 1,2-dichlorobenzene, all in presence of 0.1 M TBAP

Corrole	X	$E_{1/2ox}$	$E_{1/2red}$	Reference
Cu[T(*p*-X-P)C]	CF_3	0.89	-0.08	6
	H	0.76	-0.20	
	CH_3	0.70	-0.23	
	OCH_3	0.65	-0.24	
Cu[Br_8T(*p*-X-P)C]	CF_3	1.24	0.25	6
	H	1.14	0.12	
	CH_3	1.12	0.07	
	OCH_3	1.1	0.04	
Cu[F_8T(*p*-X-P)C]	CF_3	1.24	0.35	7
	H	1.15	0.22	
	CH_3	1.12	0.18	
	OCH_3	1.06	0.17	
Ag[T(*p*-X-P)C]	CF_3	0.91	-0.78	Manuscript in preparation
	H	0.73	-0.86	
	CH_3	0.69	-0.88	
	OCH_3	0.66	-0.91	
Au[β-Br_8-T(*p*-X-P)C]	CF_3	1.41	-0.90	This work
	H	1.29	-1.02	
	CH_3	1.27	-1.00	
	C_4H_9	1.26	-1.06	
	OCH_3	1.25	-1.09	

only effective solvent found so far, has frustrated our efforts to obtain X-ray quality crystals.

In the absence of a crystal structure, relativistic spin-orbit DFT calculations with ZORA basis sets (BP86-D/ZORA-STO-TZP; ADF 2009 [15]) were used to optimize the molecular structures of Au[TPC] and Au[Br_8TPC]. In sharp contrast to distinctly saddled Cu[TPC] [8], the calculations predicted a much flatter geometry for (the experimentally unknown) Au[TPC]. As shown in Fig. 3, the optimized geometry of Au[Br_8TPC] was also found to be much less saddled than that of Cu[Br_8TPC] [9]. Using a combination of X-ray crystallography and DFT calculations [8, 9], we have shown elsewhere that saddling in copper corroles is driven by a Cu(d_{x2-y2})-corrole(π) interaction, which is symmetry-forbidden for a planar corrole but becomes allowed under saddling. Copper corroles are thus best described as Cu^{II}-corrole$^{\bullet 2-}$. In contrast, the high energy of the Au $5d_{x2-y2}$ orbital and the relative lack of saddling in the gold case suggest a true Au(III) description.

EXPERIMENTAL

General

Ultraviolet-visible spectra were recorded on an HP 8453 spectrophotometer with dichloromethane as solvent. ^{1}H NMR spectra were recorded on a 400 MHz Mercury Plus Varian spectrometer at room temperature in 1,2-dichlorobenzene-d_4. Proton chemical shifts (δ) were referenced to residual 1,2-dichlorobenzene-d_4 (δ = 7.04 and 7.30 ppm). MALDI-TOF mass spectra were recorded on a Waters Micromass MALDI micro MX Mass Spectrometer with α-cyano-4-hydroxycinnamic acid (CHCA) as the matrix.

Cyclic voltammetry experiments were carried out at 298 K using an EG & G Model 263A potentiostat with a three-electrode system consisting of a glassy carbon working electrode, a platinum wire counterelectrode, and a saturated calomel reference electrode (SCE). Tetra-*n*-butyl ammonium perchlorate (TBAP), recrystallized from ethanol and dried in a desiccator for at least one week, was used as the supporting electrolyte. Distilled 1,2-dichlorobenzene (and, in a couple of cases, dichloromethane) was used as the solvent for cyclic voltammetry experiments. The reference electrode was separated from the bulk solution by a fritted glass bridge filled with the solvent/supporting electrolyte mixture. Pure argon was bubbled through the solution containing the gold corrole complexes for at least 2 min prior to the cyclic voltammetry experiments and the solutions were also protected from air by an argon blanket during the experiments. All half-wave potentials reported here are referenced to the SCE.

Chloroauric acid, known commercially as gold(III) chloride hydrate (99.999%), and 1,2-dichlorobenzene-d_4 (98 atom-% D) were obtained from Sigma-Aldrich and used as received. Column chromatography was performed on Matrex 35–70 silica from Millipore. The free-base H_3[Br_8T(*p*-X-P)C] corrole ligands were synthesized as described previously [10].

Common procedure for gold insertion

A 100-mL round-bottomed flask was charged with free-base H_3[Br_8T(*p*-X-P)C] (X = MeO, *n*-Bu, CH_3, H, and CF_3; 20 mg) and triethylamine (60 mL) dissolved in dichloromethane (15 mL). To the well-stirred solution was added chloroauric acid (10 equiv.) and the reaction mixture was refluxed for 0.5 h. The deep green solution of the free-base corrole turned reddish-brown within 10 min after the addition of the gold reagent. The reaction mixture was cooled to room temperature and rotary evaporated to dryness. The crude product was passed through a short silica gel column with dichloromethane as eluent (despite the limited solubility in this solvent). The resulting solution was rotary evaporated to dryness and the resulting solid was washed repeatedly with *n*-hexane, affording 54 to 65% of the pure Au[Br_8T(*p*-X-P)C] product. Yields and analytical details for the different complexes are as given below.

Au[Br_8T(*p*-CF_3-P)C]. Yield 54%. UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-4}$, $M^{-1}.cm^{-1}$) 429 (15.88), 541 (2.31), 578 (5.09). ^{1}H NMR ($C_6Cl_2D_4$): δ, ppm 8.26 (d, *J* = 7.6 Hz, 4H, 5,15-*o* or *m*-phenyl), 8.23 (d, *J* = 7.6 Hz, 2H,

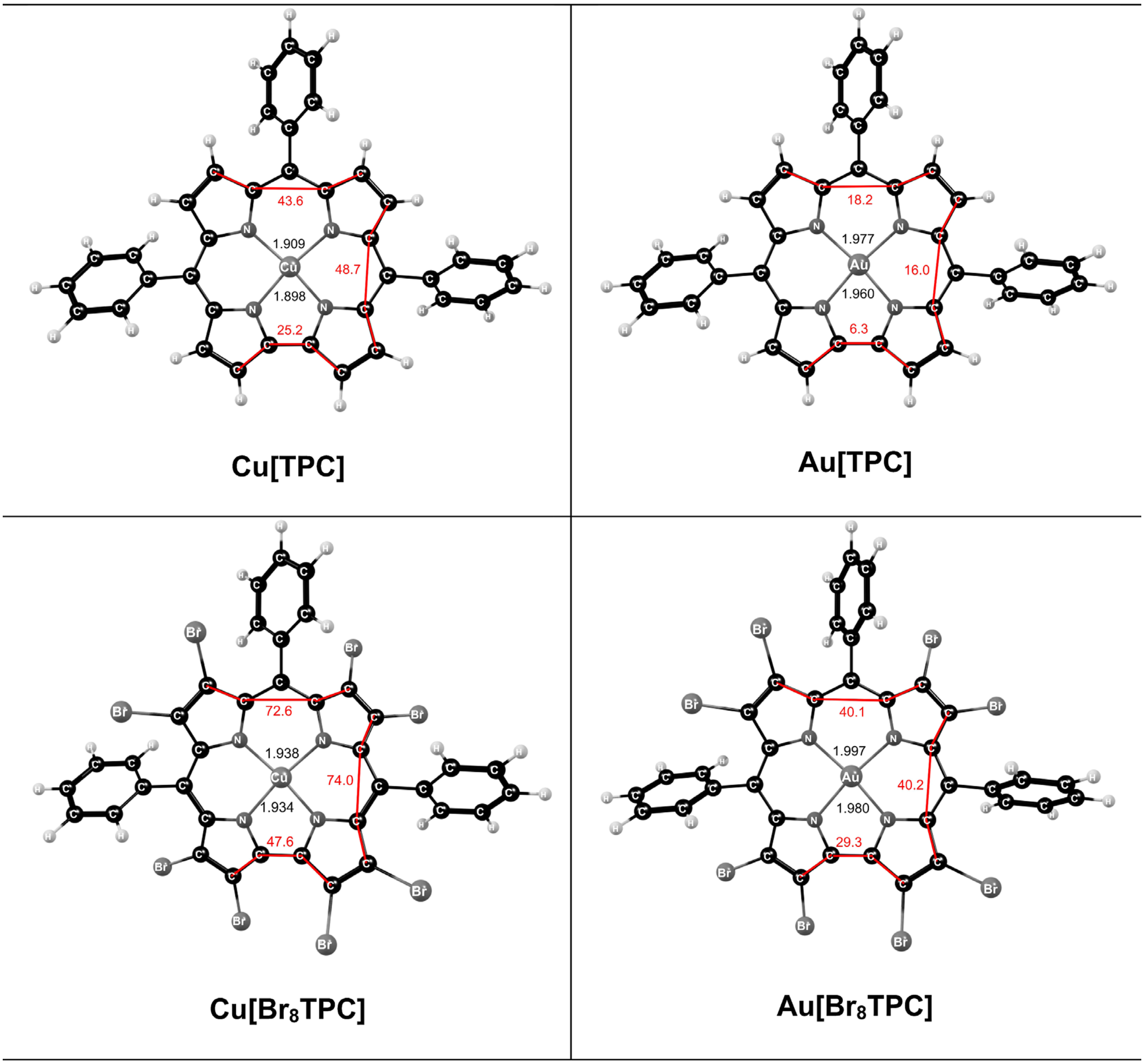

Fig. 3. Highlights of BP86/STO-TZP optimized geometries (Å, deg) of Cu and Au corroles, with key saddling dihedrals indicated in red. The Au geometries were obtained with relativistic spin-orbit calculations with ZORA basis sets, whereas nonrelativistic calculations were used for the Cu complexes

10-*o* or *m*-phenyl), 8.16 (d, $J = 7.2$ Hz, 4H, 5,15-*m* or *o*-phenyl), 8.12 (d, $J = 7.6$ Hz, 2H, 10-*m* or *o*-phenyl). MS (MALDI-TOF, major isotopomer): *m/z* $[M]^+$ 1555.83 (expt.), 1555.73 (calcd. for $C_{40}H_{12}N_4F_9Br_8Au$). Elemental analysis: C 30.10, H 1.14, N 3.93 (calcd. 30.86, 0.78, 3.60, respectively).

Au[Br$_8$TPC]. Yield 56%. UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-4}$, $M^{-1}.cm^{-1}$) 429 (12.23), 540 (1.41), 464 (9.41), 578 (3.39). ^1H NMR ($C_6Cl_2D_4$): δ, ppm 8.04–8.13 (bm, 7H, 5,15-*o* or *m*-phenyl, 10-*m* or *o*-phenyl and 10-*p*-phenyl overlapping), 7.75–7.90 (bm, 8H, 5,15-*m* or *o*-phenyl, 10-*o* or *m*-phenyl and 10-*p*-phenyl overlapping). MS (MALDI-TOF, major isotopomer): *m/z* $[M]^+$ 1351.59 (expt.), 1351.74 (calcd. for $C_{37}H_{15}N_4Br_8Au$). Elemental analysis: C 33.24, H 1.25, N 3.94 (calcd. 32.86, 1.12, 4.14, respectively).

Au[Br$_8$T(*p*-CH$_3$-P)C]. Yield 62%. UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-4}$, $M^{-1}.cm^{-1}$) 430 (11.60), 541 (1.61), 578 (3.78). ^1H NMR ($C_6Cl_2D_4$): δ, ppm 8.02 (d, $J = 8$ Hz, 4H, 5,15-*o* or *m*-phenyl), 7.99 (d, $J = 7.6$ Hz, 2H, 10-*o* or *m*-phenyl), 7.70 (d, $J = 7.2$ Hz, 4H, 5,15-*m* or *o*-phenyl), 7.66 (d, $J = 7.6$ Hz, 2H, 10-*m* or *o*-phenyl), 2.77 (s, 9H, 5,10 and 15-*p*-CH_3). MS (MALDI-TOF, major isotopomer): *m/z* $[M]^+$ 1394.15 (expt.), 1393.82 (calcd. for $C_{40}H_{21}N_4Br_8Au$). Elemental analysis: C 34.81, H 1.29, N 3.53 (calcd. 34.45, 1.52, 4.02, respectively).

Au[Br$_8$T(*p*-Bu-P)C]. Yield 54%. UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-4}$, $M^{-1}.cm^{-1}$) 430 (16.58), 542 (2.23), 578 (5.34). ^1H NMR ($C_6Cl_2D_4$): δ, ppm 8.03 (d, $J = 7.6$ Hz, 4H, 5,15-*o* or *m*-phenyl), 8.01 (d, $J = 7.6$ Hz, 2H, 10-*o* or *m*-phenyl), 7.70 (d, $J = 8.4$ Hz, 4H, 5,15-*m* or *o*-phenyl), 7.66 (d, $J = 8.4$ Hz, 2H, 5,15-*m* or *o*-phenyl), 3.03 (m, 6H, 5,10 and 15-*p*-butyl), 1.95 (m, 6H, 5,10 and 15-*p*-butyl), 1.63 (m, 6H, 5,10,15-*p*-butyl), 1.14 (m, 9H, 5,10 and 15-*p*-butyl). MS (MALDI-TOF, major isotopomer): *m/z* $[M]^+$ 1520.05 (expt.), 1520.06 (calcd. for $C_{49}H_{39}N_4Br_8Au$). Elemental analysis: C 38.53, H 2.37, N 3.76 (calcd. 38.70, 2.56, 3.69, respectively).

Au[Br$_8$T(*p*-MeO-P)C]. Yield 65%. UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-4}$, $M^{-1}.cm^{-1}$) 433 (14.70), 542 (1.06), 580 (3.56). ^1H NMR ($C_6Cl_2D_4$): δ, ppm 8.02 (d, *J* = 8 Hz, 4H, 5,15-*o* or *m*-phenyl), 7.99 (d, *J* = 8.4 Hz, 2H, 10-*o* or *m*-phenyl), 7.46 (d, *J* = 8 Hz, 4H, 5,15-*m* or *o*-phenyl), 7.42 (d, *J* = 8 Hz, 2H, 10-*m* or *o*-phenyl), 4.08 (s, 6H, 5,15-*p*-OCH_3), 4.07 (s, 3H, 10-*p*-CH_3). MS (MALDI-TOF, major isotopomer): *m/z* $[M]^+$ 1441.96 (expt.), 1441.82 (calcd. for $C_{40}H_{21}N_4O_3Br_8Au$). Elemental analysis: C 33.71, H 1.58, N 3.88 (calcd. 33.30, 1.47, 3.89, respectively).

CONCLUSION

In concluding, we would like to emphasize that the successful synthesis of gold corroles owes critically to the ease and generality of our reductive demetalation-based synthesis of free-base β-octabromo-*meso*-triarylcorrole ligands [16]. Electronic absorption, electrochemical and DFT studies already indicate fascinating variations in electronic structure among the coinage metal corroles.

Acknowledgements

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REFERENCES

1. For reviews on the coordination chemistry of porphyrins and related ligands, see: *Handbook of Porphyrin Science*, Vol. 2, Kadish KM, Smith KM and Guilard R. (Eds.) World Scientific: Singapore, 2010.
2. Aviv-Harel I and Gross Z. *Chem. Eur. J.* 2009; **15**: 8382–8394.
3. Gross Z, Galili N and Saltsman I. *Angew. Chem. Int. Ed*. 1999; **38**: 1427–1429.
4. Paolesse R, Mini S, Sagone F, Boschi T, Jaquinod L, Nurco DJ and Smith KM. *Chem. Comm*. 1999; 1307–1308.
5. Koszarna B and Gryko DT. *J. Org. Chem*. 2006; **71**: 3707–3717.
6. Wasbotten IH, Wondimagegn T and Ghosh A. *J. Am. Chem. Soc*. 2002; **124**: 8104–8116.
7. Steene E, Wondimagegn T and Ghosh A. *J. Am. Chem. Soc*. 2003; **125**: 16300–16309.
8. Alemayehu AB, Gonzalez E, Hansen LK and Ghosh A. *Inorg. Chem*. 2009; **48**: 7794–7799.
9. Alemayehu AB, Conradie J, Hansen LK and Ghosh A. *Inorg. Chem*. 2010; **49**: 7608–7610.
10. Capar C, Thomas KE and Ghosh A. *J. Porphyrins Phthalocyanines* 2008; **12**: 964–967.
11. Capar C, Hansen L.-K, Conradie J and Ghosh A. *J. Porphyrins Phthalocyanines* 2010; **14**: 509–512.
12. Ou Z, Shao J, Zhao H, Ohkubo K, Wasbotten IH, Fukuzumi S, Ghosh A and Kadish KM. *J. Porphyrins Phthalocyanines* 2004; **8**: 1236–1247.
13. The poor solubility of the Au[Br$_8$T(*p*-X-P)C] derivatives in CH_2Cl_2 may be viewed as somewhat paradoxical, given that the complexes were synthesized in that solvent.
14. Gold corroles appear to be rather stable, considerably more so than silver corroles, which demetalate easily, even by traces of acid typically present in dichloromethane: Stefanelli M, Shen J, Zhu W, Mastroianni M, Mandoj F, Nardis S, Ou Z, Kadish KM, Fronczek FR, Smith KM and Paolesse R. *Inorg. Chem*. 2009; **48**: 6879–6887.
15. a) Becke AD. *Phys. Rev.* 1988; **A38**: 3098–3100. b) Perdew JP. *Phys. Rev*. 1986; **B33**: 8822. Erratum: Perdew JP. *Phys. Rev*. 1986; **B34**: 7406. c) Dispersion corrections: Grimme S. *J. Comput. Chem*. 2006; **27**: 1787.
16. Aside from gold corroles, iridium corroles are the only other examples of third-row transition metal corroles synthesized to date: Palmer JH, Day MW, Wilson AD, Henling LM, Gross Z and Gray HB. *J. Am. Chem. Soc*. 2008; **130**: 7786–7787.