

Functionalization of Corroles: The Nitration Reaction

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The reaction of *meso*-triarylcorroles with AgNO₂ proceeds with concomitant metalation and peripheral substitution to give the corresponding nitro-substituted silver(III) corrole complex. The substitution is highly regioselective, giving only the corresponding 3-nitro derivative, among the different possible isomers. The results obtained indicate that the reaction intermediate is the π -cation radical of the complex, which is then attacked by nitrite ion. This was proven by the reaction of the copper corrole complexes with NaNO₂: in this case, the nitration reaction proceeded without the addition of an oxidant, because of the π -cation radical character of the copper complex. The reaction is also successful in the case of 2,3,17,18-tetraethyl-8,12-diacetoxymethyl-7,13-dimethylcorrole (AMCorH₃), with the formation of the *meso*-substituted silver corrole derivative (NO₂)₃AMCorAg (fully characterized by X-ray crystallography), the first of its kind to be reported. Two of the corroles are characterized by cyclic voltammetry and spectroelectrochemistry in dichloromethane, and the site of electron transfer is elucidated.

Introduction

The rich properties of porphyrins and related macrocycles make these compounds of interest for a wide range of disciplines, ranging from medicine to material science.¹ In all of these fields, the synthetic versatility of porphyrinoids is of fundamental importance, in part because it allows for fine-tuning of the macrocyclic properties and in part because it makes possible the construction of supramolecular architectures; this in turn can induce additional properties via cooperative interaction of the different macrocycles, often mimicking the complex structures of biological systems.² Among the porphyrinoids, the corroles have assumed in recent years an increasingly important role because of their

macrocycle-specific reactivity and coordination chemistry,³ which has led in some cases to applications of these compounds in the field of sensors or as catalysts.⁴ The publication of new synthetic routes for preparation of *meso*-aryl-substituted corroles from commercially available reagents⁵ has also facilitated a ready access to these compounds, which has led to rapid and impressive advancements in the field of corrole chemistry. Indeed, the previously lengthy and laborious synthetic routes to obtain β -alkylcorroles⁶ had represented a formidable obstacle to the study and use of these macrocycles.

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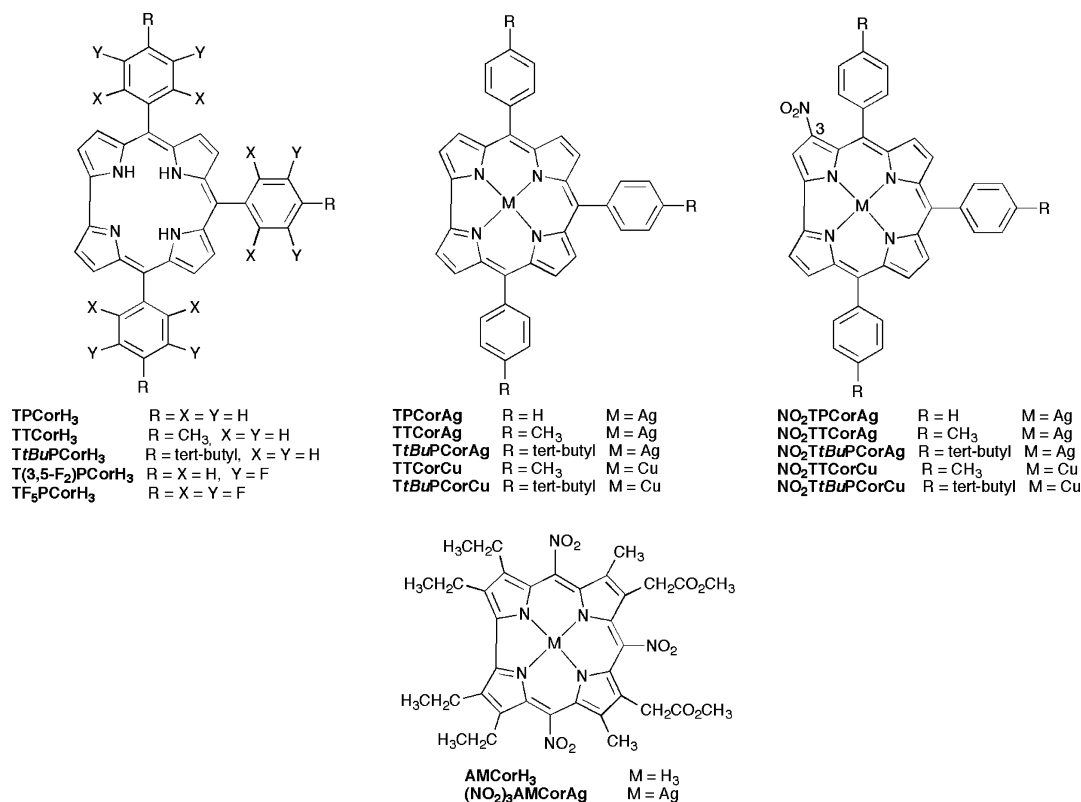
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Chart 1. Molecular Structures of the Corroles Studied



While the preparative chemistry of corroles is now well-advanced, functionalization of the β -pyrrole positions of these macrocycles still represents a significant synthetic challenge, as indicated by the fact that there are only a few examples of β -pyrrole-substituted corroles in the literature.⁷ The β -functionalization of corroles is particularly troublesome, not only because the macrocycle shows in some cases an unpredictable reactivity⁸ but also because of its lower symmetry compared with porphyrins, which can potentially lead to the formation of difficult to separate regioisomers.⁹

In the compendium of aromatic macrocycle β -functionalizations, nitration is particularly appealing because the nitro group is a useful staging point for further transformations.¹⁰ To the best of our knowledge, there is only one example in the literature of the nitration of a corrole.⁹ This reaction was carried out on a Ga complex of tri(pentafluorophenyl)corrole and has never been shown to work for a β -substituted alkylcorrole.

The substitution reactions of metal-free corroles are of potentially more general scope because the demetalation of corroles is difficult. On the other hand, functionalization of

free-base corroles is more challenging because metal-free corroles have, in the past, shown an intriguing and erratic reactivity. For example, in the case of bromination, a corrole–isocorrole tautomeric equilibrium is observed,^{5c} while hydroformylation affords an inner-core ethane-bridged macrocycle in the case of triphenylcorrole^{8b} and an aminomethene derivative in the case of β -alkylcorroles.^{8a} Finally, the reaction with Cl₄ gave the corresponding hemiporphycene by macrocyclic ring expansion.^{8c}

In the present paper, we report the nitration reaction carried out on free-base *meso*-triarylcorroles and β -alkylcorroles and characterization of the resulting silver and copper nitro derivatives (Chart 1). Our results give useful information on the mechanism of synthesis as well as provide a facile approach to the preparation of nitro-substituted corroles. We also report the first electrochemistry of silver corroles. The oxidation and reduction potentials were measured by cyclic voltammetry, and the UV–vis spectra of the electrogenerated species were characterized by thin-layer spectroelectrochemistry.

Experimental Section

General Procedure. Reagents and solvents (Sigma-Aldrich, Fluka, and Carlo Erba Reagenti) were of synthetic grade and used without further purification. Silica gel 60 (70–230 mesh) and neutral alumina (Brockmann Grade III) were used for chromatography.

¹H NMR spectra were recorded on Bruker AV300 (300 MHz) or AM400 (400 MHz) spectrometers. Chemical shifts are given in ppm relative to tetramethylsilane (TMS). UV–vis spectra were measured on a Cary 50 spectrophotometer; more precise measurements were performed on a Perkin-Elmer λ 18 spectrophotometer

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equipped with a temperature-controlled cell holder. IR spectra were recorded with a Perkin-Elmer 983G spectrometer. Mass spectra (FAB mode) were recorded on a VGQuattro spectrometer in the positive-ion mode using *m*-nitrobenzyl alcohol (Aldrich) as a matrix.

Cyclic voltammetry was carried out at 298 K by using an EG&G Princeton Applied Research (PAR) 173 potentiostat/galvanostat. A homemade three-electrode cell was used for cyclic voltammetric measurements and consisted of a platinum button or glassy-carbon working electrode, a platinum counter electrode, and a homemade saturated calomel reference electrode (SCE). The SCE was separated from the bulk of the solution by a fritted glass bridge of low porosity, which contained the solvent/supporting electrolyte mixture.

Thin-layer UV–visible spectroelectrochemical experiments were performed with a homebuilt thin-layer cell which has a light transparent platinum net working electrode.¹¹ Potentials were applied and monitored with an EG&G PAR Model 173 potentiostat. Time-resolved UV–vis spectra were recorded with a Hewlett-Packard Model 8453 diode array spectrophotometer. High purity N₂ from Trigas was used to deoxygenate the solution and kept over the solution during each electrochemical and spectroelectrochemical experiment.

Anhydrous dichloromethane (>99.8%) was obtained from Aldrich Co. and used as received for electrochemistry and spectroelectrochemistry experiments. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Sigma Chemical or Fluka Chemika Co., recrystallized from ethyl alcohol, and dried under vacuum at 40 °C for at least one week prior to use.

X-ray Crystal Data. Intensity data were collected for compound [(NO₂)₃AMCoR]Ag at *T* = 90 K using graphite-monochromated Mo K α radiation (λ = 0.71073 Å) on a Nonius KappaCCD diffractometer fitted with an Oxford Cryostream cooler. Multiscan absorption corrections led to transmission coefficients 0.837–0.935. The structure was solved by direct methods and refined by full-matrix least squares, using *SHELXL97*.¹² H atoms were visible in difference maps, but were placed in idealized positions and treated as riding. Crystal data: C₃₅H₃₆AgN₇O₁₀, fw = 822.58, dark red needle, triclinic space group *P1*, *a* = 9.7991(10) Å, *b* = 13.8489(16) Å, *c* = 14.166(2) Å, α = 62.170(4)°, β = 76.617(7)°, γ = 88.069(7)°, *V* = 1647.7(3) Å³, *Z* = 2, θ_{\max} = 30.0°, 41 575 measured reflections, 9611 independent reflections, *R*_{int} = 0.038, 8062 with *I* > 2 σ (*I*), *R* = 0.032, GOF = 1.030, 487 refined parameters, $\Delta\rho_{\max}$ = 0.77, $\Delta\rho_{\min}$ = -0.93 e·Å⁻³, deposition no. CCDC 651146.

Rotating-Frame Overhauser Enhancement Spectroscopy (ROESY) Experiment. The ROESY NMR experiment was recorded with an 80 ms spin-lock period. The 2D data sets were typically acquired with 2048 points in *t*₂, 380 points in *t*₁, and 48 scans. Data were processed and analyzed using *XWinNMR* and *Topspin* 1.2 software (Bruker Biospin). Shifted sine-bell apodization and zero-filling (1024 _ 380 real points) were applied prior to Fourier transformation, and subsequent baseline corrections were applied in one or both dimensions.

Synthesis. TPCoR₃, TTCoR₃, and TF₂PCoR₃ were prepared as previously reported.¹³ AMCoR₃ was prepared by cyclization of the corresponding *a,c*-biladiene following literature methods.⁶

5,10,15-Tris(4-*tert*-butylphenyl)corrole (TtBuPCoR₃). TtBuPCoR₃ was prepared following a literature method⁶ (yield 15%). Found: C, 84.6; H, 7.3; N, 7.9. Anal. Calcd for C₄₉H₅₀N₄:

C, 84.7; H, 7.2; N, 8.1. UV–vis: λ_{\max} (CHCl₃): 418 (ϵ 130 000), 573 (17 700), 619 (16 700), 651 (13 700) nm. ¹H NMR (300 MHz, CDCl₃): δ 8.94 (br s, 4H, β -pyrr), 8.63 (br s, 4H, β -pyrr), 8.33 (br d, 4H, phenyl), 8.13 (br d, 2H, phenyl), 7.84 (br d, 4H, phenyl), 7.79 (br d, 4H, phenyl), 1.61 (s, 27H, *p*-tBu). LRMS (FAB): *m/z* 695 (M⁺).

5,10,15-Tris(3,5-Difluorophenyl)corrole [T(3,5-F₂)PCoR₃]. T(3,5-F₂)PCoR₃ was prepared following a literature method⁶ (yield 16%). Found: C, 69.8; H, 3.0; N, 8.5. Anal. Calcd for C₃₇H₂₀F₆N₄: C, 70.0; H, 3.2; N, 8.8. UV–vis: λ_{\max} (CHCl₃): 416 (ϵ 149 000), 574 (23 400), 615 (14 000), 647 (8700) nm. ¹H NMR (300 MHz, CDCl₃): δ 9.06 (s, 2H, β -pyrr), 8.97 (s, 2H, β -pyrr), 8.67 (s, 4H, β -pyrr), 7.92 (m, 6H, phenyl), 7.75 (m, 3H, phenyl). LRMS (FAB): *m/z* 635 (M⁺).

5,10,15-Tris[(4-*tert*-butylphenyl)corrolato]silver(III) [(TtBuPCoR)Ag]. TtBuPCoR₃ (70 mg, 0.1 mmol) was dissolved in pyridine (10 mL), and silver(I) acetate (55 mg, 0.33 mmol) was added. The resulting solution was heated at 80 °C, and the progress of the reaction was monitored by thin-layer chromatography (TLC) or UV–vis spectroscopy. The color of the solution changed from green to dark red as the reaction proceeded. Upon completion, the reaction mixture was filtered through a Celite plug, the solvent was removed under vacuum, and the residue was purified by column chromatography on silica gel (CH₂Cl₂ as eluent). The first red-violet fraction was isolated and crystallized from CH₂Cl₂/MeOH, affording 52 mg (0.065 mmol, 65% yield) of (TtBuPCoR)Ag as dark red crystals. Found: C, 73.4; H, 6.1; N, 6.9. Anal. Calcd for C₄₉H₄₇AgN₄: C, 73.6; H, 5.9; N, 7.0. UV–vis: λ_{\max} (CHCl₃): 427 (ϵ 72 400), 562 (11 000), 589 (22 400) nm. ¹H NMR (300 MHz, CDCl₃): δ 9.15 (d, 2H, *J* = 4.35 Hz, β -pyrr), 9.00 (d, 2H, *J* = 4.7 Hz, β -pyrr), 8.77 (dd, 4H, β -pyrr), 8.27 (d, *J* = 8.2 Hz, 4H, phenyl), 8.17 (d, *J* = 8.2 Hz, 2H, phenyl), 7.85 (d, 4H, *J* = 8.2 Hz, phenyl), 7.81 (d, 2H, *J* = 8.2 Hz, phenyl), 1.62 (s, 18H, 5,15-*p*-tBu), 1.58 (s, 9H, 10-*p*-tBu). LRMS (FAB): *m/z* 800 (M⁺).

3-Nitro-5,10,15-triphenylcorrolato silver(III) [(NO₂TPCoR)Ag]. TPCoR₃ (53 mg, 0.1 mmol) was dissolved in CH₃CN (10 mL), and AgNO₂ (1.54 g, 10 mmol) was added. The mixture was stirred at room temperature and the progress of the reaction was monitored by UV–vis spectroscopy. The reaction was complete in about 30 min. The reaction mixture was filtered through a Celite plug, the solvent was removed on a rotary evaporator, and the residue was chromatographed on silica gel. The column was eluted with CH₂Cl₂/hexane (3:1) to afford two main fractions: the first, red-violet in color, was crystallized from CH₂Cl₂/MeOH to give (TPCoR)Ag as red crystals (5 mg, 8% yield) and had spectroscopic and analytical data in good agreement with those reported in the literature.¹⁴ The second brilliant green fraction, after evaporation, was crystallized from CH₂Cl₂/MeOH to give crystals of (NO₂TPCoR)Ag (20 mg, 30% yield). Found: C, 65.6; H, 3.3; N, 10.2. Anal. Calcd for C₃₇H₂₂AgN₅O₂: C, 65.7; H, 3.3; N, 10.4. UV–vis: λ_{\max} (CHCl₃): 433 (ϵ 50 700), 448 (sh, 48 900), 591 (28 800), 611 (26 400) nm. ¹H NMR (400 MHz, CDCl₃): δ 9.51 (s, 1H, β -pyrr), 8.95 (s, 1H, β -pyrr), 8.75 (s, 1H, β -pyrr), 8.66 (s, 1H, β -pyrr), 8.57 (s, 1H, β -pyrr), 8.52 (s, 2H, β -pyrr), 8.24 (m, 2H, phenyl), 8.13 (m, 4H, phenyl), 7.77 (m, 9H, phenyl). LRMS (FAB): *m/z* 676 (M⁺).

3-Nitro-5,10,15-tris[(4-methylphenyl)corrolato]silver(III) [(NO₂TTCor)Ag]. TTCor₃ (74 mg, 0.13 mmol) was reacted as above to give 5 mg (0.007 mmol, 6% yield) of (TTCor)Ag¹⁴ and 43 mg (46% yield) of (NO₂TTCor)Ag as green crystals. Found:

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C, 66.6; H, 3.8; N, 9.9. Anal. Calcd for $C_{40}H_{28}AgN_5O_2$: C, 66.9; H, 3.9; N, 9.7. UV-vis: λ_{max} ($CHCl_3$): 433 (ϵ 52 700), 452 (sh, 48 200), 594 (28 800), 616 (sh, 28 000) nm. 1H NMR (400 MHz, $CDCl_3$): δ 9.36 (s, 1H, β -pyrr), 8.77 (d, 1H, $J = 4.36$ Hz, β -pyrr), 8.67 (d, 1H, $J = 4.72$ Hz, β -pyrr), 8.61 (d, 1H, $J = 4.96$ Hz, β -pyrr), 8.45 (m, 3H, β -pyrr), 8.10 (d, 2H, $J = 7.8$ Hz, phenyl), 8.00 (d, 2H, $J = 7.8$ Hz, phenyl), 7.96 (d, 2H, $J = 7.8$ Hz, phenyl), 7.64 (d, 2H, $J = 7.8$ Hz, phenyl), 7.59 (d, 2H, $J = 7.8$ Hz, phenyl), 7.55 (d, 2H, $J = 7.8$ Hz, phenyl), 2.69 (s, 3H, p - CH_3), 2.66 (s, 3H, p - CH_3), 2.62 (s, 3H, p - CH_3). LRMS (FAB): m/z 718 (M^+).

3-Nitro-5,10,15-tris[(4-*tert*-butylphenyl)corrolato]silver(III) [(NO₂TtBuPCor)Ag]. TtBuPCorH₃ (180 mg, 0.26 mmol) was reacted as above to give 16 mg (0.020 mmol, 8% yield) of (TtBuPCor)Ag and 92 mg (42% yield) of (NO₂TtBuPCor)Ag as green crystals. Found: C, 69.6; H, 5.3; N, 8.0. Anal. Calcd for $C_{49}H_{46}AgN_5O_2$: C, 69.7; H, 5.5; N, 8.3. UV-vis: λ_{max} ($CHCl_3$): 431 (ϵ 46 500), 455 (sh, 41 800), 591 (sh, 23 900), 613 (24 500) nm. 1H NMR (300 MHz, $CDCl_3$): δ 9.44 (s, 1H, β -pyrr), 8.86 (d, 1H, $J = 4.3$ Hz, β -pyrr), 8.74 (d, 1H, $J = 4.7$ Hz, β -pyrr), 8.63 (d, 1H, $J = 4.9$ Hz, β -pyrr), 8.54 (d, 1H, $J = 4.3$ Hz), 8.51 (m, 2H, β -pyrr), 8.18 (d, 2H, $J = 8.2$ Hz, phenyl), 8.09 (d, 2H, $J = 8.2$ Hz, phenyl), 8.03 (d, 2H, $J = 8.2$ Hz, phenyl), 7.84 (d, $J = 8.2$ Hz, 2H, phenyl) 7.79 (d, $J = 8.2$ Hz, 2H, phenyl), 7.75 (d, $J = 8.2$ Hz, 2H, phenyl), 1.61 (s, 9H, p -*t*Bu), 1.60 (s, 9H, p -*t*Bu), 1.58 (s, 9H, p -*t*Bu). LRMS (FAB): m/z 845 (M^+).

5,10,15-Tris[(4-*tert*-butylphenyl)corrolato]copper(III) (TtBuPCor)Cu. TtBuPCorH₃ (100 mg, 0.14 mmol) was dissolved in $CHCl_3$ (100 mL), and then a solution of copper(II) acetate (60 mg, 0.33 mmol) in MeOH was added. The mixture was heated to reflux for about 2 h, and the progress of the reaction was monitored by UV-vis spectroscopy. Upon completion, the solvent was concentrated and 87 mg (80% yield) of dark brown crystals of (TtBuPCor)Cu were obtained. Found: C, 77.9; H, 6.5; N, 7.3. Anal. Calcd for $C_{49}H_{47}CuN_4$: C, 77.9; H, 6.3; N, 7.4. UV-vis: λ_{max} ($CHCl_3$): 421 (ϵ 47 700), 539 (8300), 627 (4800) nm. 1H NMR (300 MHz, $CDCl_3$): δ 7.92 (s, 2H, β -pyrr), 7.75 (m, 6H, β -pyrr and phenyl), 7.67 (s, 2H, phenyl) 7.50 (m, 6H β -pyrr and phenyl), 7.43 (m, 2H -pyrr and phenyl), 7.35 (m, 2H β -pyrr and phenyl), 1.56 (s, 18H, 5,10-*p*-*t*Bu), 1.44 (s, 9H, 15-*p*-*t*Bu). LRMS (FAB): m/z 755 (M^+).

3-Nitro-5,10,15-tris[(4-methylphenyl)corrolato]copper(III) [(NO₂TTPCor)Cu]. (TTPCor)Cu (110 mg, 0.17 mmol) was dissolved in dimethylformamide (DMF) (30 mL), and NaNO₂ (1.2 g, 17 mmol) was added. The mixture was stirred at 80 °C; the progress of the reaction was followed by examining the optical spectrum, in the Soret region, of aliquots of solution and after 90 min, the mixture was allowed to cool to room temperature and the solvent was removed using a rotary evaporation. The residue was taken up in $CHCl_3$ and washed with H₂O (3 × 50 mL portions), reduced to a small volume, and purified by chromatography on a silica gel column using CH_2Cl_2 as eluent, affording (NO₂TTPCor)-Cu (25 mg, 22% yield) as a reddish powder. Found: C, 71.1; H, 4.3; N, 10.2. Anal. Calcd for $C_{40}H_{28}CuN_5O_2$: C, 71.3; H, 4.2; N, 10.4. UV-vis: λ_{max} ($CHCl_3$): 372 (ϵ 25 000), 435 (56 000), 577 (10 300), 672 (7100) nm. 1H NMR (300 MHz, $CDCl_3$): δ 8.40 (s, 1H, β -pyrr), 7.87 (s, 1H, $J = 4.1$ Hz, β -pyrr), 7.63 (m, 7H, β -pyrr and phenyl), 7.47 (d, 1H, $J = 4.7$ Hz, β -pyrr), 7.42 (s, 2H, β -pyrr), 7.34 (s, 1H, β -pyrr), 7.32 (m, 4H, β -pyrr and phenyl), 2.48 (s, 3H, p - CH_3), 2.44 (s, 3H, p - CH_3), 2.39 (s, 3H, p - CH_3). LRMS (FAB): m/z 674 (M^+).

3-Nitro-5,10,15-tris[(4-*tert*-butylphenyl)corrolato]copper(III) [(NO₂TtBuPCor)Cu]. The reaction was carried out as above, starting from (TtBuPCor)Cu (43 mg, 0.057 mmol) and

NaNO₂ (390 mg, 5.7 mmol); the chromatographic separation was carried out on a silica gel column, using CH_2Cl_2 /hexane 3:1 as eluent. (NO₂TtBuPCor)Cu (15 mg, 33% yield) was isolated as the second fraction, and a trace of the dinitrated complex was isolated as the third fraction. Found: C, 73.6; H, 6.1; N, 8.9. Anal. Calcd for $C_{49}H_{47}CuN_5O_2$: C, 73.4; H, 5.9; N, 8.7. UV-vis: λ_{max} ($CHCl_3$): 370 (ϵ 28 400), 435 (62 000), 573 (11 700), 672 (6900) nm. 1H NMR (300 MHz, $CDCl_3$): δ 8.34 (s, 1H, β -pyrr), 7.78 (s, 1H, $J = 4.9$ Hz, β -pyrr), 7.35–7.70 (m, 17H, β -pyrr and phenyl), 1.46 (s, 9H, p -*t*Bu), 1.44 (s, 9H, p -*t*Bu), 1.43 (s, 9H, p -*t*Bu). LRMS (FAB): m/z 801 (M^+).

(5,10,15-Trinitro-2,3,17,18-tetraethyl-8,12-diacetoxymethyl-7,13-dimethylcorrolato)silver(III) [(NO₂)₃AMCor]Ag. AMCorH₃ (52 mg, 0.1 mmol) was dissolved in CH_3CN (10 mL), and AgNO₂ (1.54 mg, 10 mmol) was added. The mixture was stirred at room temperature, and the progress of the reaction was monitored by UV-vis spectroscopy. The reaction was complete in about 10 min. The reaction mixture was filtered through a plug of Celite, the solvent was removed using a rotary evaporator, and the residue was purified by chromatography on neutral alumina (Brockman grade III, CH_2Cl_2 eluant). The first brilliant orange fraction was collected and crystallized with MeOH, affording [(NO₂)₃AMCor]Ag as red crystals (40 mg, 49% yield). Found: C, 50.9; H, 4.3; N, 11.9. Anal. Calcd for $C_{35}H_{36}AgN_7O_{10}$: C, 51.1; H, 4.4; N, 11.9. UV-vis: λ_{max} (CH_2Cl_2): 421 (ϵ 78 400), 533 (15 800), 564 (24 600) nm. 1H NMR (400 MHz, $CDCl_3$): δ 4.59 (s, 4H, $-CH_2CO_2CH_3$), 4.05 (q, 4H, $-CH_2CH_3$, $J = 7.5$ Hz), 3.83 (s, 6H, $-CH_2CO_2CH_3$), 3.66 (q, 4H, $-CH_2CH_3$, $J = 7.5$ Hz), 3.23 (s, 6H, CH_3), 1.81 (t, 6H, $-CH_2CH_3$, $J = 7.5$ Hz), 1.67 (t, 6H, $-CH_2CH_3$, $J = 7.5$ Hz). LRMS (FAB): m/z 823 (M^+).

Results and Discussion

A wide range of different nitrating systems has been successfully used for the preparation of β -nitro derivatives of tetra-arylporphyrins.¹⁰ This is not the case for corroles since special attention must be paid to the maintenance of the integrity of the macrocycle under the same reaction conditions. For this reason, we did not utilize harsh nitrating systems, such as HNO₃/H₂SO₄, considering the high sensitivity of the corrole macrocycle toward oxidation. Taking into account the good results obtained in the case of porphyrins,¹⁵ we first tried using N₂O₄ for the nitration of TPCorH₃ (which was chosen as a reference system). However, no reaction was observed, and the starting material remained unchanged. We then investigated Cu(NO₃)₂ in acetic anhydride as the nitrating system; in this case, a Cu corrole complex was obtained in very low yield but there was also extensive decomposition of the starting material. The 1H NMR spectrum of the isolated product indicated a β -monosubstituted derivative, but because of the low yield, we did not attempt further characterization of this compound. Reaction with BF₄NO₂ was also investigated, but these conditions led to complete decomposition of the starting material.

Our attention therefore turned to different nitrating systems, and more satisfying results were obtained when TPCorH₃ was reacted with AgNO₂/I₂. In this case, some decomposition of the starting material was still observed, but two reaction products were isolated in moderate yields

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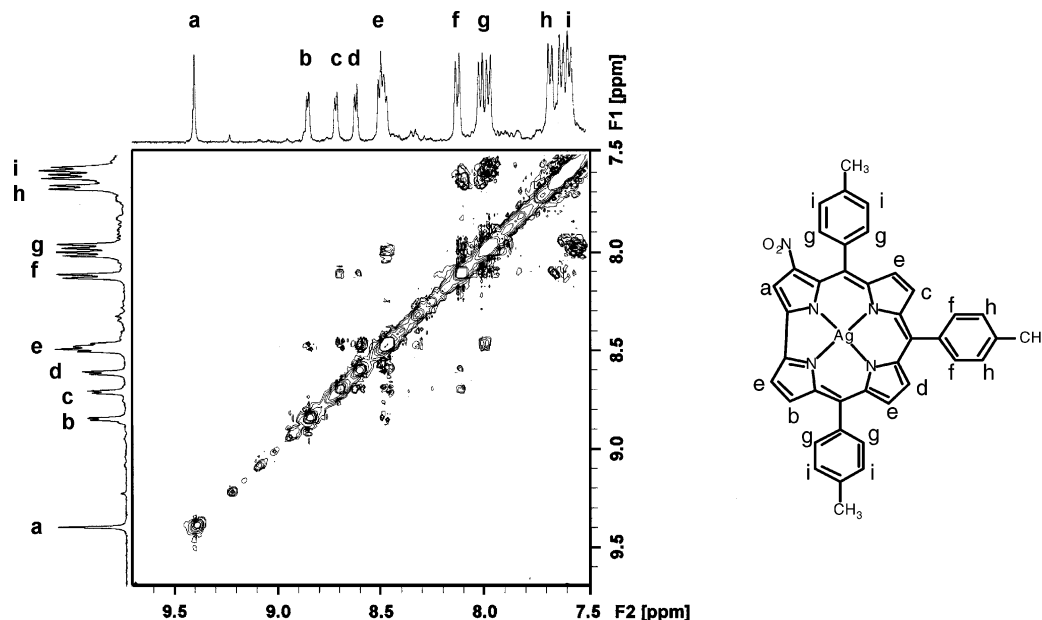


Figure 1. ROESY NMR experiment on $(\text{NO}_2\text{TTCor})\text{Ag}$.

Table 1. Influence of the Corrole Structure on the Reaction Products^a

| substrate | reaction products |
|--|--|
| TPCorH ₃ | (TPCor)Ag + (NO ₂ TPCor)Ag + open chain |
| TTCorH ₃ | (TTCor)Ag + (NO ₂ TTCor)Ag |
| TtBuPCorH ₃ | (TtBuPCor)Ag + (NO ₂ TtBuPCor)Ag |
| T(3,5-F ₂)PCorH ₃ | traces of Ag complex + open chain |
| TF ₃ PCorH ₃ | open chain |

^a Reaction conditions: AgNO_2/I_2 in CH_3CN , RT, 5–20 min under N_2 .

after chromatographic separation. The first red band, obtained in the smallest amount, was the corresponding complex (TPCor)Ag, as indicated by spectroscopic characterization and comparison with an authentic specimen of the compound prepared according to literature methods.¹⁴ The second green band was characterized as the complex $(\text{NO}_2\text{TPCor})\text{Ag}$ where coordination of the silver ion was accompanied by concomitant β -nitration of the corrole ring. This reaction seems to be regioselective, because only one product was formed; attempts to obtain single crystals of this compound were unsuccessful. The *p*-CH₃ derivative $(\text{NO}_2\text{TTCor})\text{Ag}$ is more soluble and was obtained in better yields than (TPCor)Ag, and we therefore carried out a ROESY experiment on the structurally similar corrole complex $(\text{NO}_2\text{TTCor})\text{Ag}$ to establish the site of the substitution. The spectrum obtained for $(\text{NO}_2\text{TTCor})\text{Ag}$ was shown in Figure 1 and is consistent with substitution having occurred at position 3 of the macrocycle.

This result is also in agreement with previous examples reported in the literature where the β -pyrrole position 3 is usually observed to be the most reactive site on the *meso*-triarylcorroles.⁷

With this promising result, we investigated the generality of the reaction, studying the influence of the corrole structure on the reaction products; these results are reported in Table 1. Nitration of the macrocycle is clearly favored by the presence of electron-releasing groups on the three phenyl rings. In the case of both TTCorH_3 and TtBuPCorH_3 ,

we obtained good yields of the corresponding mononitro derivatives $(\text{NO}_2\text{TTCor})\text{Ag}$ and $(\text{NO}_2\text{TtBuPCor})\text{Ag}$, with traces of the nonsubstituted complexes (TTCor)Ag and (TtBuPCor)Ag; with T(3,5-F₂)PCorH₃ and TF₃PCorH₃, we observed mostly decomposition of the corrole ring.

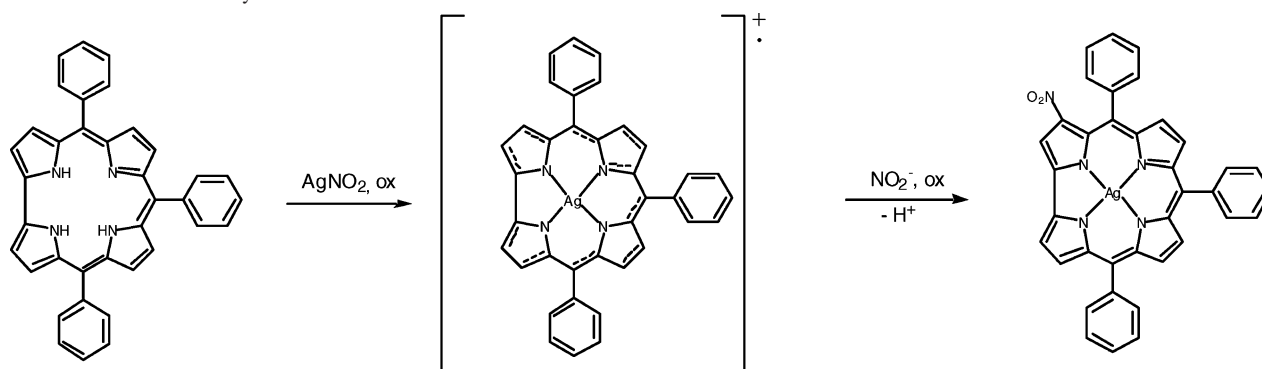
It is interesting to note at this point that I_2 is not necessary for the success of nitration. When the reaction was carried out on corrole TtBuPCorH_3 , we observed that I_2 increased the rate of the reaction, which was complete in about 5 min, but without I_2 the reaction gave the same products in 25 min. Furthermore, in the latter case, better yields of $(\text{NO}_2\text{TtBuPCor})\text{Ag}$ were observed, with no significant decomposition of the starting corrole. This intriguing result led us to further investigate the influence of specific reagents in the reaction. The silver complex (TtBuPCor)Ag was reacted with NaNO_2 under the same conditions, to check whether the presence of the silver(I) ion is necessary for the success of the reaction, but no reaction was observed, at either room temperature or under reflux in DMF, while the desired product was immediately formed when AgNO_2 was added to the reaction mixture. The same result was obtained when I_2 was added to solution instead of AgNO_2 .

The above results support the proposed reaction pathway shown in Scheme 1 where the nitrating agent is the NO_2^- ion which attacks the π -cation radical of the Ag(III) corrole that is formed by reaction with excess Ag^+ ion. At this point, a second one-electron oxidation takes place at the macrocycle and the loss of a proton restores the corrole aromaticity. The role of the silver(I) ion in macrocycle oxidation has earlier been reported for the nitration of β -octaalkylporphyrins at the meso position using AgNO_2 .¹⁶

A potential alternative to this pathway would be the possible oxidation of nitrite ion, instead of the corrole and a subsequent attack of the resulting NO_2 to give the substituted

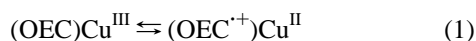
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Scheme 1. Reaction Pathway to 3-Nitro Corroles



corrole, as proposed by Gross and co-workers for a reaction involving the Ga complex of $\text{TF}_3\text{PCorH}_3$.⁹ However, this hypothesis was ruled out in the present case for two reasons. The first is that the corrole is stable in the presence of N_2O_4 , and the second reason is when the reaction is carried out under the same conditions but in the presence of urea (known to be a $\bullet\text{NO}_2$ radical trap¹⁷), the same product ($\text{NO}_2\text{TtBuPCor}$)Ag was isolated in good yield.

The presence of π -cation radical species is quite common in the coordination chemistry of corroles due to their easy oxidation and the reported “noninnocence” of the corrole macrocyclic ligand for many metal derivatives.¹⁸ One of the first reports of these radicals was by Vogel and co-workers for copper corroles;¹⁹ in this case, a temperature-dependent equilibrium, as shown in eq 1, was characterized for such species. This finding was later confirmed for corroles with triaryl substitution,²⁰ and although doubts have occasionally been raised about the correct assignment of the Cu(III) oxidation state, the presence of a radical species for the neutral corrole was recently confirmed.²¹ The presence of a radical species has also been invoked for intermediates in the spontaneous formation of dimeric corroles in solution.²²



The earlier finding that a π -radical cation species is an intermediate in the nitration reaction suggests the possibility that the reaction might be carried out, in this case, without the addition of an oxidant; were this to be true, it would further support the proposed reaction pathway. We therefore reacted the copper complex (TTCor)Cu with NaNO_2 in CH_3CN , heating the mixture to 80 °C, to shift the equilibrium in eq 1 toward the π -cation radical species at higher

temperature.¹⁹ This reaction was successful, and the mono-substituted product (NO_2TTCor)Cu was obtained along with the starting complex (TTCor)Cu and traces of a disubstituted species.

This result supports the presence of a corrole π -cation radical as the reactive species in the nitration as well as providing a convenient and facile route for the nitration reaction of corroles. It is worth mentioning that to the best of our knowledge, this is the first nonspectroscopic evidence for the π -radical cation nature of such a complex.

To further examine the scope of the reaction, we examined nitration of the β -alkylcorroles, a reaction that had not before been reported. We first reacted AMCorH_3 with AgNO_2 in CH_3CN and after 10 min observed complete disappearance of the starting corrole; TLC showed the formation of a single reaction product, and spectroscopic characterization indicated complete substitution at the meso position to give $[(\text{NO}_2)_3\text{AMCor}]\text{Ag}$. The structural identity was confirmed by single-crystal X-ray crystallography (Figure 2).

The Ag atom has square-planar coordination, with Ag–N distances in the range of 1.9478(15)–1.9752(15) Å, those to the directly linked pyrroles shorter than the other two by 0.025 Å. Likewise, the N1–Ag–N4 bite angle in the five-membered chelate ring is 79.95(7)°, while those in the six-membered chelate rings are in the range of 92.10(7)–95.62(6)°. The corrole ring deviates slightly from planarity, with a small saddle distortion. Opposite peripheral C atoms C2, C3, C12, and C13 lie out of the best plane of the 23 corrole atoms by an average of 0.253 Å, while the other four, C7, C8, C17, and C18, lie out-of-plane by an average of –0.238 Å. The Ag atom is nearly in the plane, with a deviation of –0.0195(2) Å.

Electrochemistry in CH_2Cl_2 . Two representative Ag(III) corroles, (TtBuPCor)Ag and ($\text{NO}_2\text{TtBuPCor}$)Ag, were electrochemically investigated to determine the ease of oxidation/reduction, the stability of electrogenerated products, and the effect of nitration on the redox reactions. (TtBuPCor)Ag undergoes two oxidations, and a single well-defined reduction in CH_2Cl_2 containing 0.1 M TBAP, as seen in Figure 3a. All three reactions involve reversible one-electron transfers located at $E_{1/2} = 0.72, 1.20, \text{ and } -0.87 \text{ V vs SCE}$.²³

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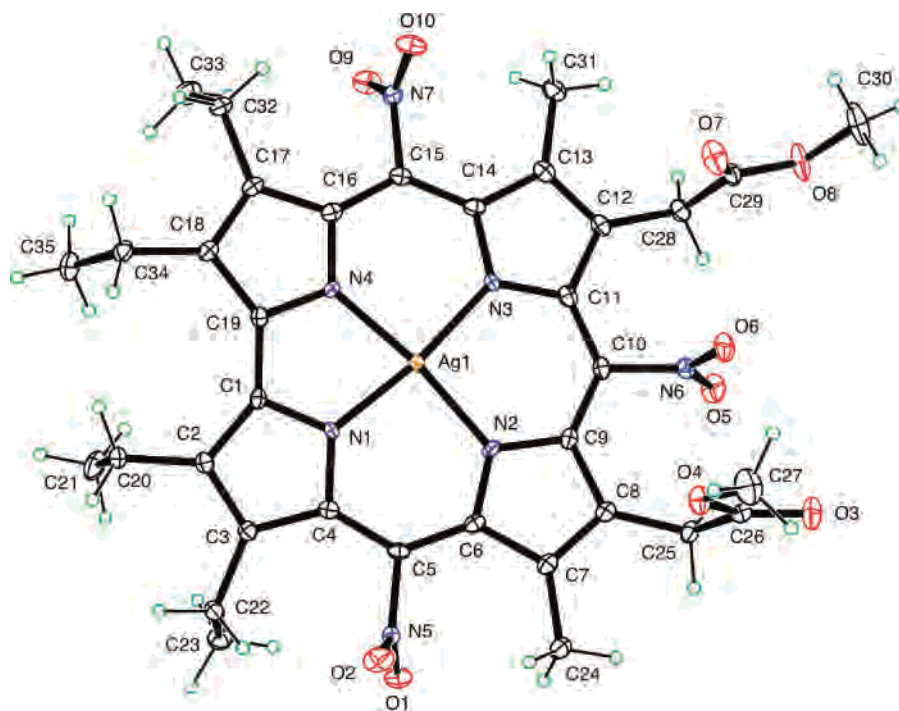


Figure 2. X-ray molecular structure of $[(\text{NO}_2)_3\text{AMCor}]\text{Ag}$ with 50% ellipsoids.

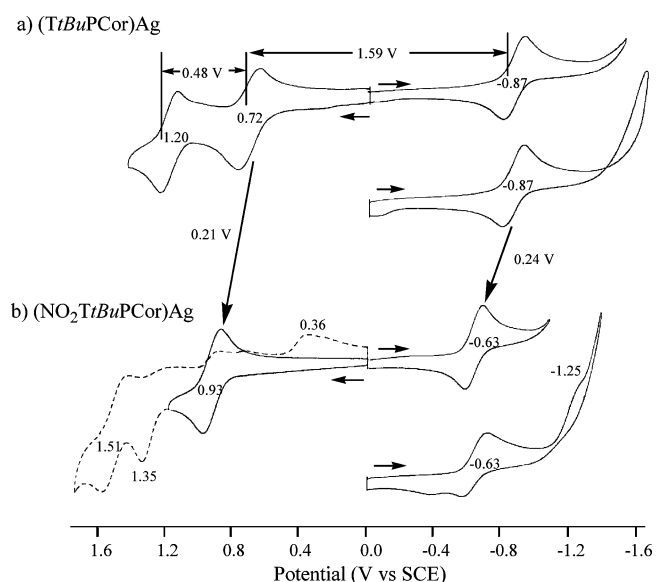


Figure 3. Cyclic voltammograms of $(\text{TtBuPCor})\text{Ag}^{\text{III}}$ and $(\text{NO}_2\text{TtBuPCor})\text{Ag}^{\text{III}}$ in CH_2Cl_2 containing 0.1 M TBAP at a scan rate of 0.1 V/s.

The electrochemical data in Figure 3a can be compared to results obtained for $(\text{TPP})\text{Ag}^{\text{II}}$ under similar solution conditions,²⁴ where TPP = the dianion of tetraphenylporphyrin. The $(\text{TPP})\text{Ag}^{\text{II}}$ complex is reduced to its $\text{Ag}(\text{I})$ form at -1.01 V vs SCE in CH_2Cl_2 and oxidized to $[(\text{TPP})\text{Ag}^{\text{III}}]^+$ at 0.59 V. Both reactions of the porphyrin occur at more negative potentials than those for the reduction and oxidation of $(\text{TtBuPCor})\text{Ag}^{\text{III}}$, but the HOMO–LUMO gap of 1.60 V for $(\text{TPP})\text{Ag}^{\text{II}}$ is identical within experimental error to the 1.59 V gap observed in the case of $(\text{TtBuPCor})\text{Ag}^{\text{III}}$. The HOMO–LUMO gap is the same for silver corroles and the

corresponding porphyrins, so they have almost identical Soret band maxima. For example, the corroles $(\text{TPCor})\text{Ag}$, $(\text{TtBuPCor})\text{Ag}$ and $(\text{TTCor})\text{Ag}$ have a Soret band at 423 – 424 nm, while the porphyrins $(\text{TPP})\text{Ag}$ and $(\text{TTP})\text{Ag}$ have a Soret band at 422 – 423 nm.²⁴ Porphyrins and related macrocycles with silver(IV) are unknown, and the two reversible oxidations of $(\text{TtBuPCor})\text{Ag}^{\text{III}}$ can be reasonably assigned as generating a $\text{Ag}(\text{III})$ corrole π -cation radical and dication. The $\Delta E_{1/2}$ value of 480 mV between the two oxidations is larger than that observed for most porphyrins²⁵ but smaller than what has been reported for other corroles that are oxidized at the conjugated π -ring system, for example, the metal derivatives of $\text{Cu}(\text{III})$,²⁶ $\text{Sn}(\text{IV})$,²⁷ and $\text{P}(\text{V})$.²⁸

$(\text{NO}_2\text{TtBuPCor})\text{Ag}$ also undergoes a reversible one-electron reduction at -0.63 V and three oxidations at 0.93 , 1.35 , and 1.51 V as seen in Figure 3b. The second oxidation of $(\text{NO}_2\text{TtBuPCor})\text{Ag}$ is coupled to a chemical reaction following electron abstraction, as shown by the dashed line in the cyclic voltammogram. The product of the doubly oxidized corrole may be an isocorrole, as indicated by the reversible third oxidation at $E_{1/2} = 1.51$ V and the new re-reduction peak at $E_{\text{pc}} = 0.36$ V, but this was not investigated in the current study.

The addition of an NO_2 group to one of the β -pyrrole positions of $(\text{TtBuPCor})\text{Ag}$ was expected to result in a

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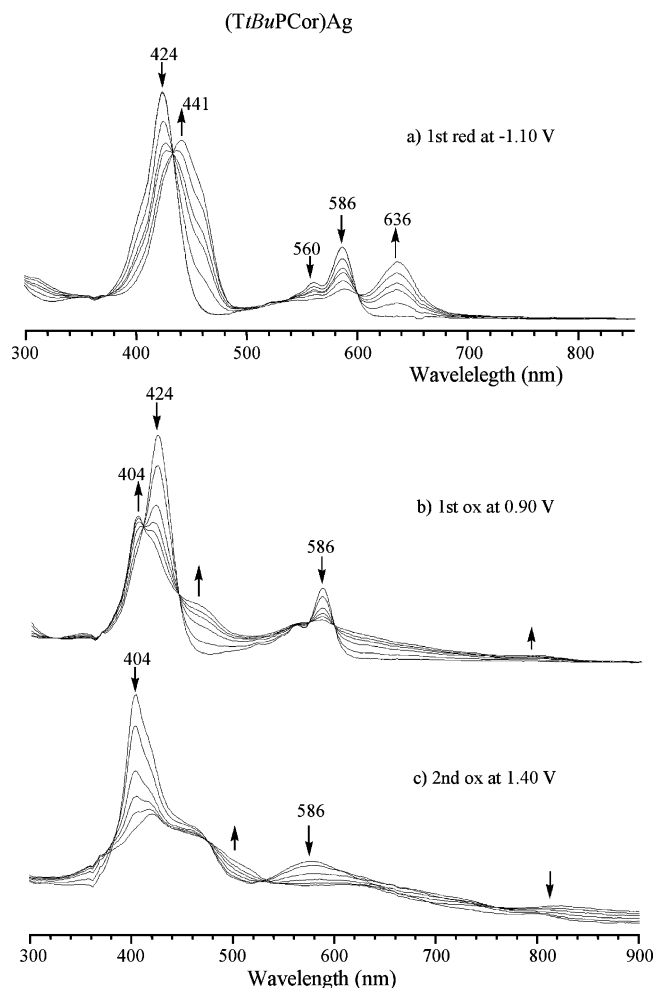


Figure 4. UV-vis spectral changes of $(\text{TtBuPCor})\text{Ag}^{\text{III}}$ obtained during controlled potential electrolysis at (a) -1.10 V, (b) 0.90 V, and (c) 1.40 V in CH_2Cl_2 , 0.1 M TBAP.

positive shift of $E_{1/2}$ for both the oxidation and reduction, with the difference in potentials between the nitrated and non-nitrated compounds depending upon the site of electron transfer. A shift in $E_{1/2}$ of 300 – 400 mV has often been observed for ring-centered reductions of TPP complexes upon nitration,²⁹ but the shift in $E_{1/2}$ is less for metal-centered reductions, for example, the $\text{M}^{\text{III/II}}$ reductions of porphyrins with Au (260 mV)³⁰ or Co (190 mV)³¹ metal centers. Thus, the 240 mV difference in $E_{1/2}$ between the reduction of $(\text{TtBuPCor})\text{Ag}$ and $(\text{NO}_2\text{TtBuPCor})\text{Ag}$ is quite consistent with the expected $\text{Ag}^{\text{III/II}}$ reaction of the corrole.

The 210 mV separation in $E_{1/2}$ between the first oxidation of $(\text{TtBuPCor})\text{Ag}$ (0.72 V) and $(\text{NO}_2\text{TtBuPCor})\text{Ag}$ (0.93 V) is also consistent with what has been reported for porphyrin ring-centered oxidations, example being given for derivatives with Cu, Zn, and Mg central metal ions.²⁹ This fact,

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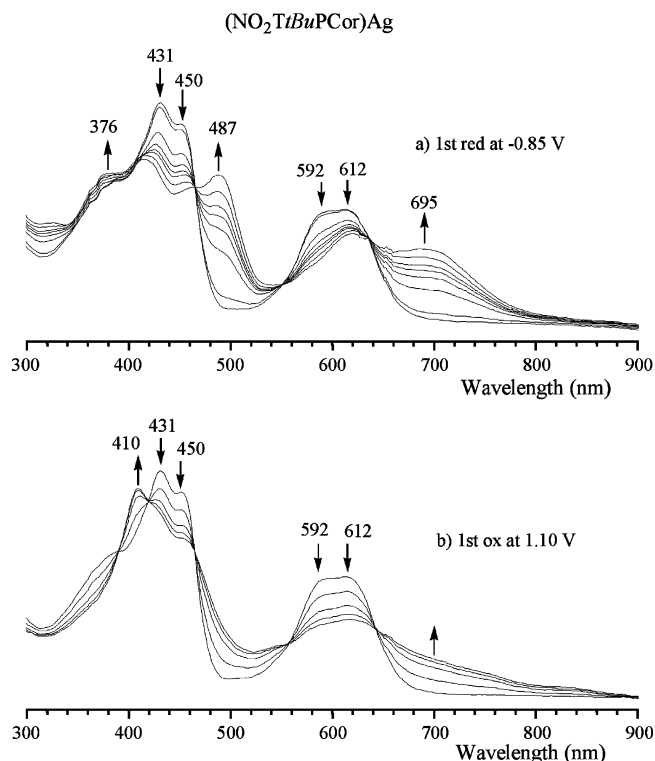
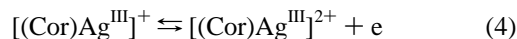
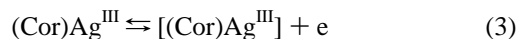
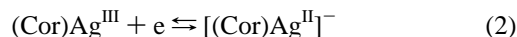


Figure 5. UV-vis spectral changes of $(\text{NO}_2\text{TtBuPCor})\text{Ag}^{\text{III}}$ obtained during (a) the first reduction at -0.85 V and (b) the first oxidation at 1.10 V in CH_2Cl_2 , 0.1 M TBAP.

combined with the above-described results for the reduction of the two corroles, provides strong indirect evidence for the electron-transfer reactions given in eqs 2–4, and this was confirmed by thin-layer UV-vis spectroelectrochemistry.



Examples of the spectral changes which occur during the reduction and oxidation of $(\text{TtBuPCor})\text{Ag}$ and $(\text{NO}_2\text{TtBuPCor})\text{Ag}$ are illustrated in Figures 4 and 5, respectively. The initial $(\text{TtBuPCor})\text{Ag}$ complex in CH_2Cl_2 has a Soret band at 424 nm and two visible bands at 560 and 586 nm. Upon the first reduction at -1.10 V, the Soret band shifts to 441 nm and an intense visible band grows in at 636 nm (Figure 4a). There are no characteristic π -anion radical bands in the spectrum of the singly reduced species, and the spectral changes are consistent with the $\text{Ag}^{\text{III/II}}$ process shown in eq 2. The spectra of the singly and doubly oxidized corrole are also consistent with the stepwise formation of a π -cation radical and dication, the former being characterized by a decreased intensity Soret band and a broad band between 700 and 850 nm. The spectrum of the neutral corrole could be fully recovered when the potential was set back to 0.0 V, thus indicating a reversibility of the processes and a good stability of the singly and doubly oxidized forms of the corrole in CH_2Cl_2 .

Functionalization of Corroles

Similar spectral changes were seen during the first reduction and first oxidation of $(\text{NO}_2\text{TtBuPCor})\text{Ag}$ in CH_2Cl_2 . The spectrum of neutral $(\text{NO}_2\text{TtBuPCor})\text{Ag}$ differs from that of neutral $(\text{TtBuPCor})\text{Ag}$ under the same experimental conditions (Figure 5), but the spectra of the singly reduced and singly oxidized forms of the corrole are consistent with electrogeneration of $[(\text{NO}_2\text{TtBuPCor})\text{Ag}^{\text{II}}]^-$ and $[(\text{NO}_2\text{TtBuPCor})\text{Ag}]^+$, respectively, as shown in eqs 2 and 3.

Conclusions

We have reported a general method for the nitration of corroles both at the β and meso positions of the macrocycle by reaction of the free-base corrole with AgNO_2 . The reaction proceeds with high selectivity for substitution on the *meso*-triarylcorroles, and it is also successful in the case of β -alkylcorroles. Although the reaction was carried out on the free-base corrole, the reaction product was always the corresponding substituted silver(III) complex. The results obtained indicate that the reaction intermediate is the π -cation radical of the complex, which is then attacked by nitrite ion.

This was proven by reaction of the copper corrole complexes with NaNO_2 ; in this case, the nitration reaction proceeded without the addition of an oxidant, because of the π -cation radical character of the copper complex.

This Article presents also the first study on electrochemistry and spectroelectrochemistry of silver corrole complexes, and elucidates the site of electron transfer and the influence of the nitro group. The nitro-substituted complexes represent useful intermediates for the construction of more complex molecular architectures based on corroles, a topic of ongoing research in our laboratories.

Acknowledgment. This research was supported by the Italian MUR (FIRB project RBNE01KZZM), the U.S. National Science Foundation (K.M.S. Grant CHE-0296012), and the Robert A. Welch Foundation (K.M.K. Grant E-680).

Supporting Information Available: CIF file of $[(\text{NO}_2)_3\text{AMCor}]\text{Ag}$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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