Inorg. Chem. **2008**, *47*, 11680–11687

Inorganic Chemistry

Article

β-Nitro Derivatives of Germanium(IV) Corrolates

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Received July 29, 2008

The reaction between germanium(IV) *meso*-triphenylcorrolates and nitrate salts affords the corresponding β-nitro substituted corroles in good yield. Chromatographic separation of the crude reaction mixtures enables isolation of a μ-oxo dimer along with the corresponding monomers bearing a hydroxy or methoxy group at an axial position of the germanium central metal ion. Depending on the reaction conditions, mono- or dinitro substituted complexes can be obtained. The substitution is highly regioselective in each case, giving only the 3-nitro or 3,17-dinitro derivative among the different possible isomers. Five of the synthesized complexes were examined by cyclic voltammetry and UV−visible spectroelectrochemistry in dichloromethane, and the dinitro μ-oxo dimer is structurally characterized.

Introduction

The new millennium was an important turning point for corroles, because it signaled the beginning of an impressive increase in published literature on these compounds.[1] From this point of view, it is interesting to note that the corrole macrocycle (Figure 1) is not a novelty in the porphyrinoid field but was first reported in the early 1960s by Johnson and Kay when they were attempting to find a synthetic route to vitamin B_{12}.[2] In recent years, the development of facile and efficient synthetic routes for the preparation of triarylcorroles from commercially available precursors has been a driving force for the increased "popularity" of this macrocycle,[1,3] in part because it made the corroles more accessible for study by a wider number of research groups and in part because of the intriguing chemical character of this macrocycle.

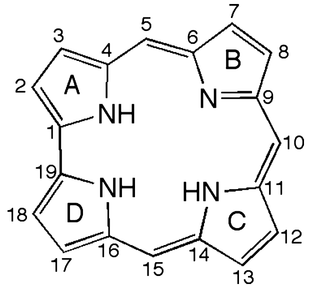

Figure 1. Molecular structure of corrole.

The coordination chemistry of corroles differs in several respects from that of the more ubiquitous porphyrins.[4] A characteristic feature of the corrole is the contracted macrocycle with its trianionic ligand character, an attribute that induces a stabilization of the central metal ion in higher formal oxidation states than in the case of the corresponding porphyrins whose macrocycles are dianionic ligands.[5] The natural consequence of a higher central metal oxidation state

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10.1021/ic801421a CCC: $40.75

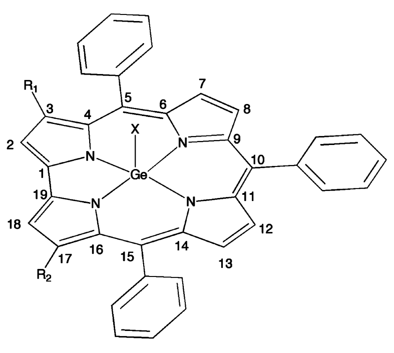
and a higher electron density in the corroles leads to the so-called "noninnocent" character of the macrocycle as a ligand, which has sometimes complicated the interpretation of its coordination and electrochemical behavior.[6] On the other hand, this behavior is important for exploiting the applications of metallocorroles in several areas such as, for example, catalysis or chemical sensing, where coordination interaction is fundamental for the working mechanism of the organic material.[1,7] For all of these applications, it is also important to develop synthetic routes for the functionalization of corrole, where different substituents are introduced at the peripheral positions of the molecular framework.[3d,8] This is of particular importance for the construction of more elaborate molecular architectures and for fine-tuning the properties of the macrocycle itself.

The lower molecular symmetry of corroles compared with porphyrins makes their functionalization especially challenging, because it introduces the problem of regioisomer formation.[8] In this regard, corroles have generally shown an unexpected regioselectivity,[9] with pyrroles A and D (and in particular positions 3- and 17-) being more reactive than pyrroles B and C (see Figure 1); this fact has been successfully exploited to obtain regioselectively substituted corroles in good yields.[3d]

Our laboratories have been interested for some time in elucidating the reactivity of corroles in different substitution reactions, and we have generally used the free-base macrocycle as a starting material.[3d,10] This choice was due both to the lack of facile protocols for the demetalation of metallocorroles and to the interesting reactivity shown by the free-base form of the corrole in these reactions. However, in some cases, the exploitation of a metal complex is necessary to drive a particular reaction towards the expected products. From this point of view, we have recently shown that it is possible to demetalate corroles under controlled conditions,[11] and this opportunity may allow novel important perspectives for the functionalization of the macrocycle, perhaps reaching the versatility obtained in the case of porphyrins.[12]

Among the known metallocorroles, derivatives of germanium(IV)[13] offer several features that make them advantageous for exploiting various corrole functionalization reactions. For example, the Ge(IV) corrolates are quite stable and can be used under a variety of substitution reaction conditions; they are also diamagnetic, allowing for facile characterization of their reaction products. Furthermore, we have recently shown that these metallomacrocycles may be isolated in pure form after bromination of the macrocycle at the β-pyrrole positions.[14] This is not a trivial result, because bromination is a reaction which has been difficult to control with corroles, and in the past, only the fully brominated product has been isolated in good yield.[15]

Chart 1. Molecular Structures of the Synthesized Corroles



TPCorrGe(OCH$_3$)	R^1 = R^2 = H; X = OCH$_3$
TPCorrGe(OH)	R^1 = R^2 = H; X = OH
(TPCorrGe)$_2$O	R^1 = R^2 = H; X = OGeTPCorr
(3-NO$_2$)TPCorrGe(OCH$_3$)	R^1 = NO$_2$; R^2 = H; X = OCH$_3$
(3-NO$_2$)TPCorrGe(OH)	R^1 = NO$_2$; R^2 = H; X = OH
[(3-NO$_2$)TPCorrGe]$_2$O	R^1 = NO$_2$; R^2 = H; X = [(3-NO$_2$)TPCorrGe]O
(3,17-NO$_2$)$_2$TPCorrGe(OCH$_3$)	R^1 = R^2 = NO$_2$; X = OCH$_3$
[(3,17-NO$_2$)$_2$TPCorrGe]$_2$O	R^1 = R^2 = NO$_2$; X = [(3,17-NO$_2$)$_2$TPCorrGe]O

In this paper, we have expanded our earlier studies of Ge(IV) corrolates to include the nitration reaction, which is a fundamentally useful functionalization reaction of tetrapyrrole macrocycles[12] and of aromatic molecules in general. The synthesized corroles are shown in Chart 1. Three of the compounds containing a nitrated macrocycle are examined as to their electrochemistry and spectroelectrochemistry in nonaqueous media, and these data are compared to the redox behavior of a related monomer and μ-oxo dimer not having the added NO$_2$ groups. The oxidation and reduction potentials were measured by cyclic voltammetry, and UV−visible spectra of the electrogenerated species were characterized by thin-layer spectroelectrochemistry. One compound, the dinitro μ-oxo dimer, is also structurally characterized.

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Experimental Section

Reagents and solvents (Sigma-Aldrich, Fluka, and Carlo Erba Reagenti) for synthesis and purification of Ge(IV) corrolates 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.

^{1}H NMR spectra were recorded on a Bruker AV300 (300 MHz) spectrometer. Chemical shifts are given in parts per million relative to tetramethylsilane (TMS). UV−vis spectra were measured on a Cary 50 spectrophotometer; more precise measurements were performed on a Perkin-Elmer λ18 spectrophotometer equipped with a temperature-controlled cell holder. Mass spectra (FAB mode) were recorded on a VGQuattro spectrometer in the positive-ion mode using *m*-nitrobenzyl alcohol (NBA, Aldrich) as a matrix.

Cyclic voltammetry was carried out at 298 K 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 homemade thin-layer cell which has a light transparent platinum net working electrode. Potentials were applied and monitored with an EG&G PAR Model 173 potentiostat. Time-resolved UV−visible spectra were recorded with a Hewlett-Packard Model 8453 diode array spectrophotometer. High-purity N_2 from Trigas was used to deoxygenate the solution and kept over the solution during each electrochemical and spectroelectrochemical experiment.

Dichloromethane (CH_2Cl_2) and pyridine (py) were obtained from Aldrich Co. and were 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 a vacuum at 40 °C for at least one week prior to use.

X-Ray Crystal Data. Diffraction data were collected on a Nonius KappaCCD diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and an Oxford Cryostream low-temperature device. Crystal data for $[3,17\text{-}(NO_2)_2TPCorrGe]_2O$: $C_{74}H_{42}N_{12}O_9Ge_2 \cdot 2CHCl_3$, monoclinic, space group $P2_1/n$, $a = 18.634(2)$, $b = 16.1855(15)$, $c = 23.728(4)$ Å, $\beta = 94.528(6)°$, $V = 7134.0(15)$ Å^3, $Z = 4$, $D_{calcd} = 1.515$ g cm^{-3}, $\mu = 1.136$ mm^{-1}, $T = 90$ K, 66 866 reflections collected with $\theta_{max} < 26.4°$, 14 509 independent reflections ($R_{int} = 0.046$) which were used in all of the calculations. The chloroform molecules are disordered, and their contribution to the structure factors was removed using SQUEEZE [Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7−13]. Final residuals (for 874 parameters) were R_1 [$I > 2\sigma(I)$] = 0.049 and wR_2 (all data) = 0.134, CCDC 692211.

Synthesis. $TPCorrH_3$ and $TPCorrGe(OCH_3)$ were prepared as previously reported.[3,14]

Nitration of $TPCorrGe(OCH_3)$. Method A. A solution of $TPCorrGe(OCH_3)$ (62 mg, 0.1 mmol) in CH_2Cl_2 (35 mL) was treated with 3.5 mL of a solution of $LiNO_3$ (80 mg) in AcOH (4 mL) and Ac_2O (2.3 mL), and the mixture was heated at reflux. The color of the solution turned from purple to green, and after 5 min, a TLC examination revealed no starting material; the mixture was diluted with CH_2Cl_2 (35 mL), washed three times with water, dried over Na_2SO_4, and the solvent then evaporated. The residue was chromatographed on a neutral alumina column (Brockmann grade III, 100 g); elution with CH_2Cl_2 afforded a first green fraction, which was crystallized from CH_2Cl_2/hexane to give blue-green crystals of $[3\text{-}(NO_2)TPCorrGe]_2O$ (22 mg, 34% yield). A second green fraction was obtained after eluting with $CHCl_3$; crystallization from CH_2Cl_2/hexane afforded $3\text{-}NO_2TPCorrGe(OH)$ as dark crystals (10 mg, 15% yield). $[3\text{-}(NO_2)TPCorrGe]_2O$ was successively washed with 4 M HCl, dried over Na_2SO_4, and then added to the $3\text{-}NO_2TPCorrGe(OH)$ fraction dissolved in CH_2Cl_2; crystallization from CH_2Cl_2/MeOH afforded red-green crystals of $3\text{-}NO_2TPCorrGe(OCH_3)$ (30 mg, 45% yield).

$[3\text{-}(NO_2)TPCorrGe]_2O$. Anal found for $C_{74}H_{44}Ge_2N_{10}O_5$: C, 68.6; H, 3.5; N, 10.5. Calcd: C, 68.4; H, 3.4; N, 10.8%. UV−vis (CH_2Cl_2): λ_{max}, nm 422 (ε 125 300), 601 (35 500). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.31 (s, 2H, β-pyrr.), 8.52 (d, 2H, $J = 4.4$ Hz, β-pyrr.), 8.43 (d, 2H, $J = 4.8$ Hz, β-pyrr.), 8.37 (d, 2H, $J = 4.8$ Hz, β-pyrr.), 8.09 (overlapping dd, 4H, β-pyrr.), 8.02 (d, 2H, $J = 4.8$ Hz, β-pyrr.), 7.5−7.9 (m, 30H, phenyls). LRMS (FAB): *m/z* 1298 (M$^+$).

$3\text{-}NO_2TPCorrGe(OH)$. Anal. found for $C_{37}H_{23}GeN_5O_3$: C, 67.6; H, 3.2; N, 10.5. Calcd: C, 67.5; H, 3.5; N, 10.6%. UV−vis (CH_2Cl_2): λ_{max}, nm 426 (ε 73 900), 607 (22 800). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.71 (s, 1H, β-pyrr.), 9.25 (d, 1H, $J = 4.1$ Hz, β-pyrr.), 9.09 (d, 1H, $J = 4.8$ Hz, β-pyrr.), 9.00 (d, 2H, $J = 4.6$ Hz, β-pyrr), 8.75 (dd, 2H, β-pyrr.), 8.40−7.65 (m, 15H, phenyls), −4.02 (br s, 1H, OH). LRMS (FAB): *m/z* 658 (M$^+$).

$3\text{-}NO_2TPCorrGe(OCH_3)$. Anal. found for $C_{38}H_{25}GeN_5O_3$: C, 67.6; H, 3.6; N, 10.5. Calcd: C, 67.9; H, 3.8; N, 10.4%. UV−vis (CH_2Cl_2): λ_{max}, nm 426 (ε 73 900), 607 (22 800). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.72 (s,1H, β-pyrr.), 9.24 (d, 1H, $J = 4.3$ Hz, β-pyrr.), 9.09 (d, 1H, $J = 4.8$ Hz, β-pyrr.), 9.00 (d, 2H, $J = 4.4$ Hz, β-pyrr), 8.76 (d, 1H, $J = 5.2$ Hz, β-pyrr.), 8.75 (d, 1H, $J = 5.1$ Hz, β-pyrr.), 7.6−8.4 (m, 15H, phenyls), −0.62 (s, 3H, OCH_3). LRMS (FAB): *m/z* 672 (M$^+$).

Method B. $TPCorrGe(OCH_3)$ (90 mg, 0.144 mmol) and $NaNO_3$ (32 mg, 0.36 mmol) were dissolved in 15 mL of acetic anhydride and stirred at 45 °C, and then 6 mL of acetic acid was added. The solution color became deep green, and after 30 min, TLC showed no more starting material in the reaction mixture. The solvent was evaporated and the residue dissolved in CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$; the organic phase was concentrated and chromatographed on a neutral alumina (Brockmann grade III) column (100 g); a first green fraction was obtained using CH_2Cl_2 as the eluant, and the residue was crystallized from CH_2Cl_2/hexane to give green crystals of $[3,17\text{-}(NO_2)_2TPCorrGe]_2O$ (12 mg, 12% yield); elution with $CHCl_3$ afforded a second green band that was crystallized from CH_2Cl_2/MeOH to give directly $3,17\text{-}(NO_2)_2TPCorrGe(OCH_3)$ (36 mg, 35% yield).

$[3,17\text{-}(NO_2)_2TPCorrGe]_2O$. Anal. found for $C_{74}H_{42}Ge_2N_{12}O_9$: C, 63.9; H, 3.1; N, 11.9. Calcd: C, 64.0; H, 3.0; N, 12.1%. UV−vis: λ_{max}, nm (CH_2Cl_2): 422 (ε 126 900), 601 (41 500). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.20 (s, 2H, β-pyrr.), 8.48 (d, 2H, $J = 4.9$ Hz, β-pyrr.), 8.07 (d, 2H, $J = 4.9$ Hz, β-pyrr.), 7.4−8.0 (m, 15H, phenyls). LRMS (FAB): *m/z* 1388 (M$^+$).

$3,17\text{-}(NO_2)_2TPCorrGe(OCH_3)$. Anal. found for $C_{38}H_{24}GeN_6O_5$: C, 63.2; H, 3.5; N, 11.5. Calcd: C, 63.6; H, 3.4; N, 11.7%. UV−vis: λ_{max}, nm (CH_2Cl_2): 428 (ε 43 700), 449 (sh., 38 200), 630 (21 100). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.57 (s, 2H, β-pyrr.), 8.97 (d, 2H, $J = 5.0$ Hz, β-pyrr.), 8.67 (d, 2H, $J = 5.0$ Hz, β-pyrr.), 7.7−8.2 (m, 15H, phenyls), −0.63(s, 3H, OCH_3). LRMS (FAB): *m/z* 717 (M$^+$).

Results and Discussion

Synthesis and Characterization. Preparation of the Ge(IV) corrolates was performed by reacting the free-base macrocycle with $GeCl_4$ in refluxing DMF.[14] It was earlier reported that this reaction affords two complexes, the μ-oxo dimer $(TPCorrGe)_2O$ and the corresponding monomer, TPCorrGe(OH), both resulting from the facile hydrolysis of the Ge−Cl bond on an initial TPPCorrGeCl intermediate.[14] The monohydroxide and μ-oxo dimer species were both converted into the corresponding methoxide complex, $TPCorrGe(OCH_3)$, which was previously used as a model compound for the bromination reaction.[14] $(TPCorrGe)_2O$ was first treated with dilute HCl and then crystallized from CH_2Cl_2/CH_3OH, while the direct crystallization of TPCorrGe(OH) was sufficient to afford $TPCorrGe(OCH_3)$ in quantitative yield.

The successful nitration of free-base corroles using $AgNO_2$ as a nitrating reagent in CH_3CN was recently reported.[16] Following this promising result, we attempted the same nitrating system in the case of $TPCorrGe(OCH_3)$, but this reaction led mostly to the formation of ring-opened species, with only traces of the desired macrocyclic substituted product(s) being obtained. Open-chain products were also earlier observed when reacting the pentafluorophenyl derivative $TF_5PCorrH_3$ with $AgNO_2$.

The above failure to get the desired nitrated product led us to explore alternative approaches, and we decided to use the mild nitrating system, $LiNO_3/Ac_2O/AcOH$ in CH_2Cl_2, which was reported to be successful in the nitration of nonaromatic Ni corrole complexes.[17] Although in our previous work electrophilic nitrating reagents did not give satisfying results in terms of functionalizing the free-base corrole (due to decomposition of the starting material[16]), both the mild conditions and the presence of a corrole metal complex were promising for the fate of the reaction. In this case, the reaction was successful, and after 5 min, no starting material remained in the crude mixture, as evidenced by TLC analysis.

The chromatographic separation performed on neutral alumina afforded two main products. Spectral characterization of the first fraction indicated that the μ-oxo dimer of a monosubstituted Ge derivatives had been formed; FAB mass spectrometry showed a molecular peak corresponding to a the μ-oxo Ge(IV) complex, and the ^1H NMR spectrum showed a singlet at 9.31 ppm, indicating substitution at a β-pyrrolic position of the macrocycle. The second fraction was identified as the corresponding monosubstituted monomer bearing a hydroxyl group at the Ge(IV) axial position. Treatment of the μ-oxo dimer with dilute HCl also led to a mixture of monomeric corroles, one with a Cl^- axial ligand and the other with bound OH^-. This fraction was combined with the hydroxide derivative directly obtained from the reaction and crystallized from CH_2Cl_2/CH_3OH to give the corresponding methoxy corrole in 45% yield.

The regioselectivity of the reaction is worth noting because only one isomer is obtained from the β-substitution reaction. According to the high reactivity shown at the 3- position in analogous triarylcorrole functionalizations[3d] and to the spectral characterization, in particular ^1H NMR characterization that supports the site of this substitution at the 3- position of the macrocycle,[18] these Ge(IV) derivatives can be confidently identified as the 3-nitro substituted species, as further confirmed by the results described later in the manuscript. Unfortunately, all attempts to obtain single crystals of these derivatives failed, thereby thwarting their unambiguous characterization. It should be noted that the regioselectivity observed is the same reported for the nitration reaction of the Ga complex of the 5,10,15-tris(pentafluorophenyl)corrole.[8]

To explore the possibility of obtaining poly substitution products, we elected to use reaction conditions moderately more severe than those exploited earlier, using a molar excess of $NaNO_3$ in $Ac_2O/AcOH$. The choice was successful, and a chromatographic separation of the crude mixture in this case afforded two main products. The first band showed traces of a compound that spectral characterization identified as being identical with $[3\text{-}(NO_2)TPCorrGe]_2O$. The subsequent fraction afforded again a μ-oxo dimer of a disubstituted Ge corrole derivative, as shown by FAB mass spectrometry. The ^1H NMR spectrum indicated a symmetrical pattern for the substitution, indicating formation of the 3,17-dinitro μ-oxo dimer. Single crystals of this compound were obtained by slow diffusion of hexane into a diluted dichloromethane solution, and an X-ray crystal structure determination unambiguously confirmed the compound to be $[3,17\text{-}(NO_2)_2TPCorrGe]_2O$. Its structure is shown in Figure 2.

In the μ-oxo dimer, Ge1 lies 0.483(2) and Ge2 lies 0.398(2) Å out of their basal N_4 planes, toward the interior of the molecule. Ge2 has a long intermolecular distance of 2.921(2) Å to an O atom of a nitro group trans to the bridging O, while Ge1 has no such axial interaction to either other Ge dimers or solvent molecules.

The Ge−N distances in the five-membered chelate rings are in the range 1.919(3)−1.929(3) Å, longer than the others, being 1.902(3)−1.914(3) Å; Ge−O1 distances are 1.735(2) Å for Ge1 and 1.738(2) Å for Ge2, and the Ge−O−Ge angle is distinctly nonlinear, being 157.61(15)°. This causes the two N_4 planes to form a dihedral angle of 18.10(8)°. The distance between the Ge atoms is 3.834(1) Å, and the distance between the two N_4 centers is 4.220 Å. Overall, the dimeric molecule has approximate C_2 symmetry, with the two corrole rings twisted with respect to each other by 61.5° about the Ge···Ge vector. The individual corroles are nonplanar, distorted somewhat into saddle conformations. The 23 atoms of the corrole ring coordinating Ge1 exhibit a mean deviation of 0.102 Å from coplanarity, with a maximum of 0.238(3) Å. For the corrole coordinating Ge2, these values are 0.120 and 0.291(3) Å.

The structure of $[3,17\text{-}(NO_2)_2TPCorrGe]_2O$ is quite similar to that of the corresponding compound lacking the nitro groups.[14] In that structure, the Ge−N distances are in the

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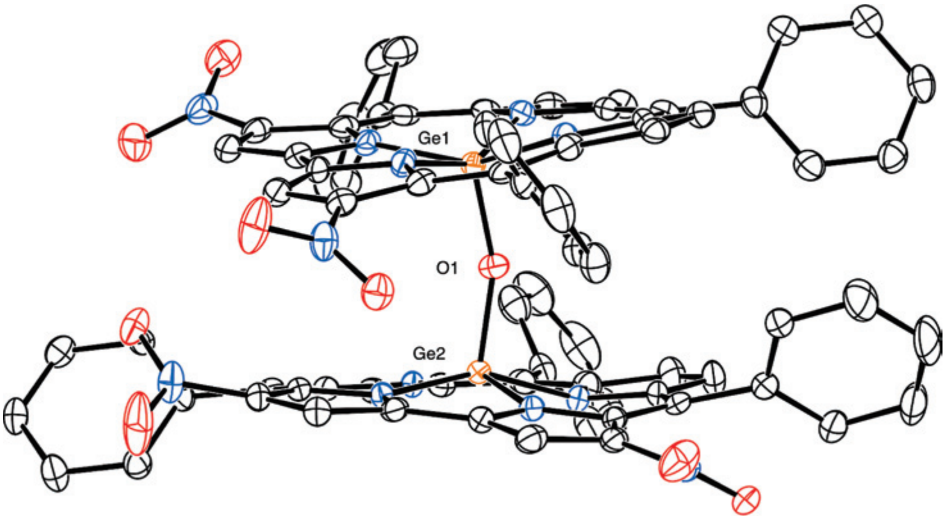

Figure 2. Molecular structure of $[3,17\text{-}(NO_2)_2TPCorrGe]_2O$, with 50% ellipsoids. H atoms are not shown.

range 1.881(9)−1.930(9) Å, and the Ge−O distances are in the range 1.718(11)−1.773(13) Å in two independent molecules. Dihedral angles between the N_4 planes in that structure are 19.4(6) and 19.9(5)°, comparable to those in $[3,17\text{-}(NO_2)_2TPCorrGe]_2O$. However, its Ge−O−Ge angles, 147.3(5) and 149.0(4)°, are significantly smaller than in the current structure, leading to smaller Ge•••Ge distances, 3.349(2) and 3.359(2) Å.

It should be noted that the additional fraction in the reaction mixture was the disubstituted monomer $3,17\text{-}(NO_2)_2TPCorrGe(OH)$, which was directly converted into the corresponding methoxy derivative, $3,17\text{-}(NO_2)_2\text{-}TPCorrGe(OCH_3)$, by crystallization from CH_2Cl_2/CH_3OH. The substitution is highly regioselective, and only the 3,17-disubstituted isomer was isolated, the total yield of the reaction being around 50%, thus indicating that the starting complex is sufficiently stable under the given reaction conditions. Also in this case, the 3,17- substitution pattern observed is identical to that reported in the case of the Ga complex of 5,10,15-tris(pentafluorophenyl)corrole,[8] confirming this corrole regioselectivity in the nitration reactions.

The UV−vis spectra of the mono- and dinitrosubstituted complexes in dichloromethane are shown in Figure 3. The compounds all exhibit a Soret band at around 425 nm and a broad Q-band close to 600 nm. Introduction of nitro substituents at the peripheral positions of the macrocycle of the triphenylcorrole induce significant variations in the spectral features of the starting $TPCorrGeOCH_3$, as illustrated in the figure. Upon substitution, both the Soret and Q absorption bands are red-shifted and considerably broadened. There is also a significant increase of the relative Q-band intensity. The addition of a second nitro group does not induce similar changes in the absorption spectra. As already observed in the case of unsubstituted Ge(IV) triphenylcorrolates,[14] $[3\text{-}(NO_2)TPCorrGe]_2O$ and $[3,17\text{-}(NO_2)_2\text{-}TPCorrGe]_2O$ (Figure 4) show Soret bands which are higher in intensity than those of the corresponding monomer, but the corresponding shift to shorter wavelengths is in this case less than that observed for the unsubstituted species. The broadening of the Q bands, on the other hand, is not accompanied by similar band shifts. Both features seem to indicate a smaller degree of interaction among the two macrocycles in the μ-oxo dimer. Both $[3\text{-}(NO_2)TP\text{-}CorrGe]_2O$ and $[3,17\text{-}(NO_2)_2TPCorrGe]_2O$ are unstable upon dilution, and at concentrations lower than 10^{-6} M, their spectra slowly revert to those of the corresponding monomers.

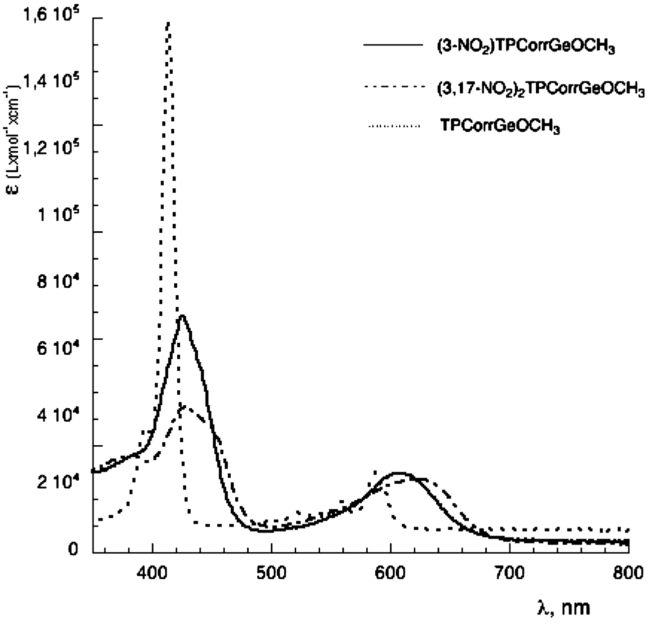

Figure 3. UV−visible spectra of the mono-Ge(IV) corrolates.

Electrochemistry. Figures 5 and 6 and Figure S1 (Supporting Information) illustrate cyclic voltammograms of the five investigated Ge(IV) corrolates, while Table 1 summarizes redox potentials of these compounds in CH_2Cl_2 containing 0.1 M TBAP and also includes the data for three related compounds of Ge(IV), one a derivative of a Ge complex of the 5,10,15-tris(pentafluorophenyl)corrole and the other two of Ge(IV) tetraphenylporphyrin derivatives. Two one-electron reductions, located at $E_{1/2} = -1.36$ V and $E_{pc} = -1.95$ V and two one-electron oxidations, at $E_{1/2} = 0.79$ and 1.22 V, are observed for $TPCorrGe(OCH_3)$ in CH_2Cl_2. In contrast, up to three reductions and three oxidations can

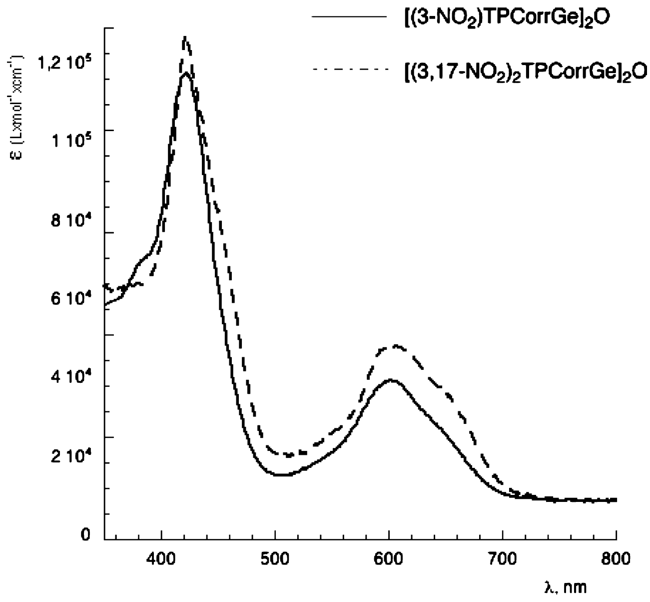

Figure 4. UV−visible spectra of the bis-Ge(IV) corrolates.

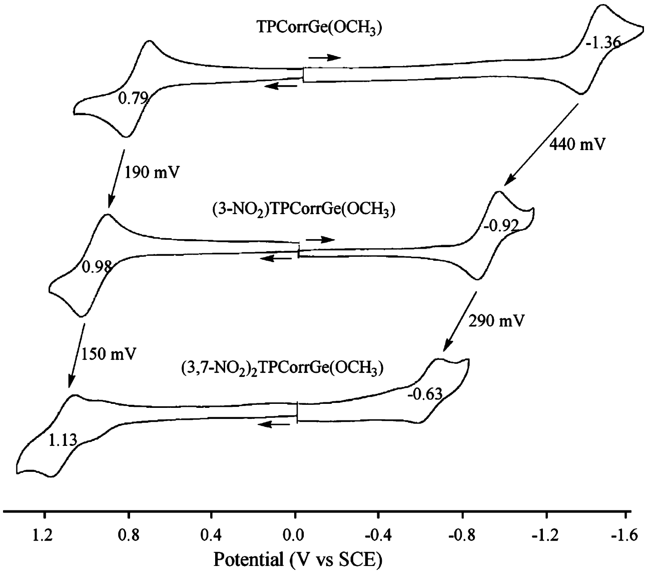

Figure 5. Cyclic voltammograms showing the first reduction and first oxidation of mono-Ge(IV) corrolates with zero, one, or two NO_2 groups at the *β* position(s) of the macrocycle. Measuring was made in CH_2Cl_2 containing 0.1 M TBAP.

be observed for the 3-nitro and 3,17-dinitro derivatives under the same solution conditions (Table 1 and Figure S1, Supporting Information).

The nitro functionality is a strong electron-withdrawing group that shows a strong electronic interaction with the porphyrin macrocycle and can affect both the HOMO and LUMO energy levels.[19] Generally, the addition of a single nitro substituent on the *β*-pyrrole position of a metallotetraphenylporphyrin such as (TPP)M, where M = 2H, Cu, Mg, or Zn, will lead to a 330−380 mV positive shift in $E_{1/2}$ for the first reduction but only a 100−110 mV positive shift in the first oxidation as compared to the same compound without the nitro groups.[20−22] A similar trend is observed for the investigated Ge(IV) corrolates; the redox potentials of the compounds are all positively shifted when one or two nitro groups are introduced onto the *β*-pyrrole position of the macrocycle, and the reductions are more effected than the oxidations by nitration. For example, in the case of mononitration, the first reduction is positively shifted by 440 mV, from $E_{1/2} = -1.36$ V for TPCorrGe(OCH_3) to −0.92 V for (3-NO_2)TPCorrGe(OCH_3). At the same time, the first oxidation is shifted by 190 mV, from 0.79 V for TPCorrGe(OCH_3) to 0.98 V for (3-NO_2)TPCorrGe(OCH_3) (see Figure 5).

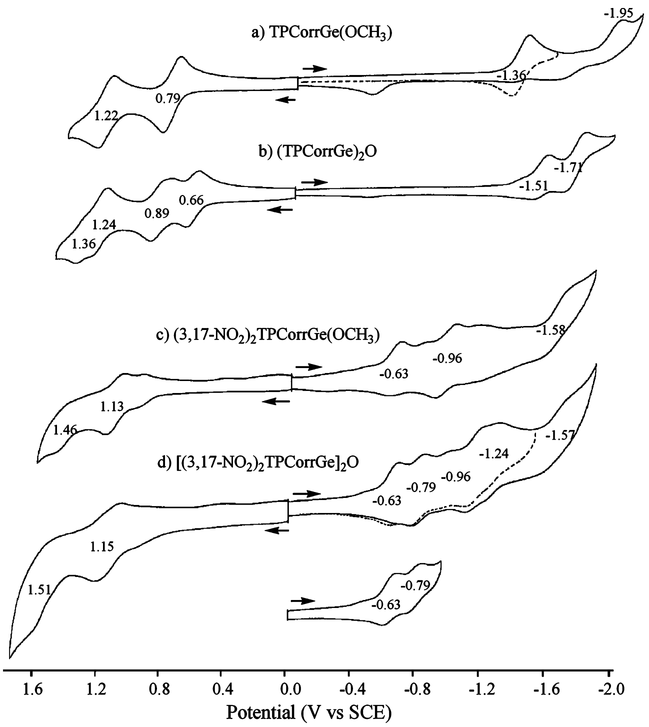

Figure 6. Cyclic voltammograms of mono-Ge corrolates and bis-Ge(IV) corrolates in CH_2Cl_2 containing 0.1 M TBAP.

The first reduction and first oxidation of the monomeric dinitro corrole, (3,17-NO_2)$_2$TPCorrGe(OCH_3)), are located at $E_{1/2} = -0.63$ and 1.13 V, respectively, in CH_2Cl_2 and 0.1 M TBAP. Compared with (3-NO_2)TPCorrGe(OCH_3), the $E_{1/2}$ of the 3,17-dinitro derivative is only shifted by 290 mV for reduction and 150 mV for oxidation (Figure 5). Thus, the addition of a second nitro group to the macrocycle decreases the effect of nitration on the redox potentials under the same experimental conditions.

The potential difference between the first reduction and first oxidation of TPCorrGe(OCH_3) in CH_2Cl_2 and 0.1 M TBAP (the HOMO−LUMO gap) is 2.15 V for (Table 1 and Figure S1, Supporting Information), a separation within the range of values previously reported for other metallocor-

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Table 1. Half -Wave Potential (V vs SCE) of Ge(IV) Corroles in CH_2Cl_2, 0.1 M TBAP

	oxidation			reduction			$\Delta E_{1/2}$[a]
compound	third	second	first	first	second	third	(V)
TPCorrGe(OCH_3)		1.22	0.79	−1.36	−1.95[b]		2.15
(3-NO_2)TPCorrGe(OCH_3)	1.60	1.32	0.98	−0.92	−1.18		1.90
(3,17-NO_2)$_2$TPCorrGe(OCH_3)		1.46	1.13	−0.63	−0.96	−1.58	1.76
(TPCorrGe)$_2$O		1.36, 1.24	0.89, 0.66	−1.51[c]	−1.71[c]		2.17
[(3,17-NO_2)$_2$TPCorrGe]$_2$O		1.51[c]	1.15[c]	−0.63, −0.79	−0.96, −1.24	−1.57	1.78
TF_5PCorrGe(OH)[d]			1.13	−0.99			2.13
(TPP)Ge(ClO_4)$_2$[e]			1.48	−0.69	−1.56		2.17
(TPP)Ge(OH)$_2$[e]		1.46[b]	1.15	−1.09	−1.56		2.24

[a] The HOMO−LUMO gap (potential difference between the first oxidation and first reduction). [b] Irreversible potential peak at a scan rate of 0.1 V/s. [c] Two overlapping one-electron processes. [d] Data taken from ref 13b, TF_5PCorr = 5,10,15-tris(pentafluorophenyl)corrole. [e] In PhCN, data taken from ref 24.

roles.[12,23] It is also similar to the HOMO−LUMO gap of the Ge(IV) porphyrins (TPP)Ge(ClO_4)$_2$ and (TPP)Ge(OH)$_2$ where $\Delta E_{1/2} = 2.17$ and 2.24 V, respectively[24] (see Table 1).

Upon nitration, the HOMO−LUMO gap decreases to 1.90 V for (3-NO_2)TPCorrGe(OCH_3) and 1.76 V for (3,17-NO_2)$_2$TPCorrGe(OCH_3), respectively (see Table 1 and Figure S1, Supporting Information).

The μ-oxo dimer, (TPCorrGe)$_2$O, undergoes two reversible reductions and four reversible one-electron oxidations within the potential range of dichloromethane (Figure 6b). Each reduction process involves two overlapping one-electron additions, and a total of four electrons are added to the two corrole macrocycles of the dimer upon scanning the potential from 0.0 to −2.0 V versus SCE in CH_2Cl_2 and 0.1 M TBAP.

In contrast to the reduction, the first one-electron oxidation does not occur at the same potential for each macrocycle of the μ-oxo dimer, thus indicating an interaction between two equivalent redox active sites on the molecule.[19] The half-wave potentials are located at $E_{1/2} = 0.66$ and 0.89 V, resulting in a 0.23 V potential separation between the two processes, the first of which gives a μ-oxo dimer with one singly oxidized macrocycle and the second a dimer where both macrocycles are oxidized by one electron. Stepwise oxidations have also been reported for μ-oxo iron(III) porphyrinates[25] and porphycenates[26] where the $\Delta E_{1/2}$ values between each process range from 0.19 to 0.26 mV. The second oxidation of each macrocycle in (TPCorrGe)$_2$O also occurs at different half-wave potentials, being 1.24 and 1.36 V as seen in Figure 6b. These results indicate that an interaction also exists between the two singly oxidized corrole macrocycles of the μ-oxo dimer.

Compared with (TPCorrGe)$_2$O, different electrochemical behavior is seen for the dinitro μ-oxo dimer under the same solution conditions. Both the first and second oxidations of [(3,17-NO_2)$_2$TPCorrGe]$_2$O involve two overlapping one-electron transfer steps which occur at the same potential for each macrocycle. This is not the case for the first two reductions of the compound, which occur in well-separated one-electron steps (see Figure 6d). This is consistent with an interaction between the two neutral and singly reduced corrole rings of the 3,17-dinitro μ-oxo Ge(IV) dimer, but not between the two oxidized macrocycles, which are equivalent and noninteracting under the given solution conditions.

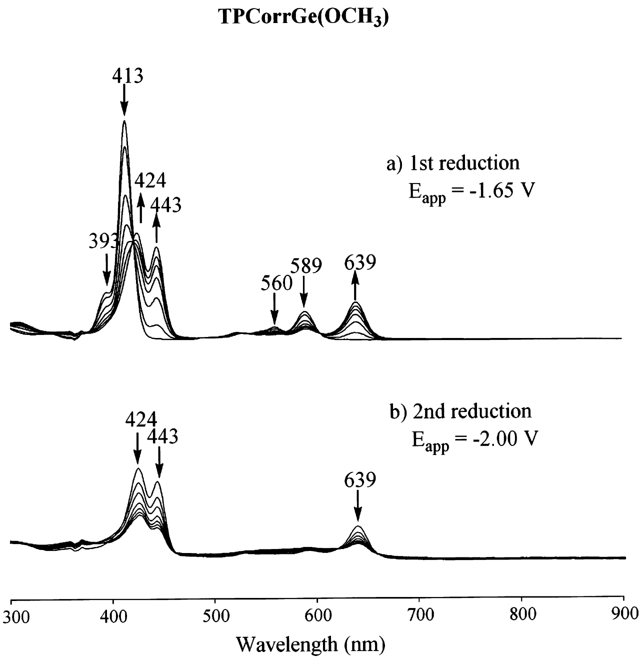

Figure 7. UV−vis spectral changes of TPCorrGe(OCH_3) during reduction at a controlled potential of (a) −1.65 and (b) −2.00 V in CH_2Cl_2 containing 0.1 M TBAP.

Spectroelectrochemistry. Thin-layer UV−visible spectroelectrochemistry was carried out under the same solution conditions as for the cyclic voltammetry measurements. Changes in the UV−visible spectra upon reduction or oxidation of the different corroles are shown in Figures 7−9 and Figures S2−S4, Supporting Information).

Upon the first controlled potential reduction of TPCorrGe(OCH_3) at −1.65 V, the Soret band at 413 nm and the visible bands at 560 and 589 nm decrease in intensity while two low-intensity Soret bands and a broad visible band grow in at 424, 443, and 639 nm (Figure 7a). The intensity of the newly formed bands then decreases upon the second controlled potential reduction at −2.00 V (Figure 7b). The stepwise reduction products are assigned as a π-anion radical and dianion. The spectral changes obtained during the first and second oxidations are illustrated in Figure 8. The Soret and visible bands decrease in intensity, but no new bands in

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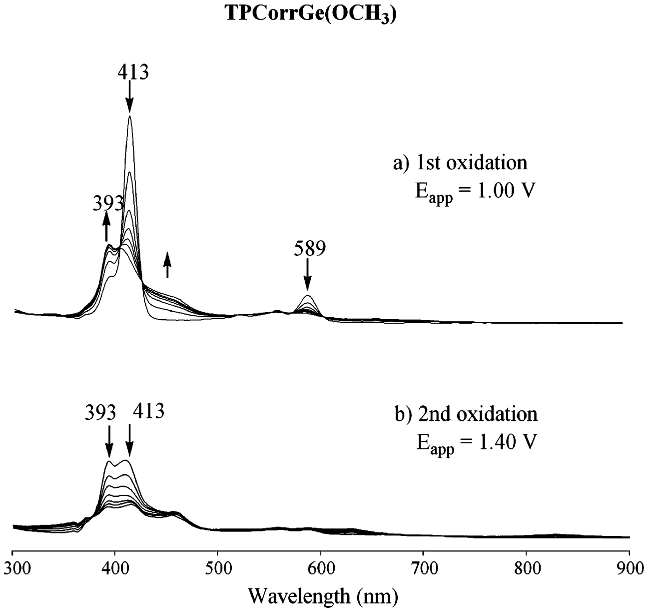

Figure 8. UV−vis spectral changes of TPCorrGe(OCH_3) during oxidation at a controlled potential of (a) 1.00 and (b) 1.40 V in CH_2Cl_2 and 0.1 M TBAP.

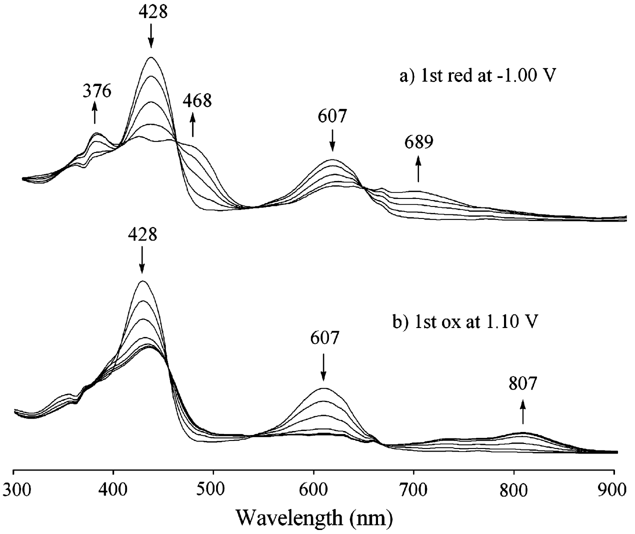

Figure 9. UV−vis spectral changes of (3-NO_2)TPCorrGe(OCH_3) during (a) reduction at −1.00 V and (b) oxidation at 1.10 V in CH_2Cl_2 and 0.1 M TBAP.

the visible region are seen upon the first oxidation at 1.00 V (Figure 8a). Similar spectra have been assigned to corrole cation radicals,[27] and a π-cation radical is assigned in the present study. The spectra of the doubly oxidized species are shown in Figure 8b and assigned to a dication.

Similar spectral changes are observed upon controlled potential reduction and oxidation of $(TPCorrGe)_2O$ (Figures S2 and S3, Supporting Information). The reduction at −1.65 V occurs at both macrocycles simultaneously and leads to $[TPCorr^{-\bullet}Ge{-}O{-}GeTPCorr^{-\bullet}]^{2-}$ as the spectrally detected product. The first two one-electron oxidations of the starting compound at 0.80 and 1.00 V lead to a stepwise formation of $[TPCorr^{+\bullet}Ge{-}O{-}GeTPCorr]^{+}$ and $[TPCorr^{+\bullet}Ge{-}O{-}GeTPCorr^{+\bullet}]^{2+}$ in the thin-layer cell.

The initial spectrum of the 3-nitro and 3,17-dinitro derivatives before oxidation or reduction differs from that of TPCorrGe(OCH_3) in CH_2Cl_2 containing 0.1 M TBAP. The Soret and visible bands of 3-nitro and 3,17-dinitro derivatives are both broad (Figures 9 and Figure S4, Supporting Information). Due to the electron-withdrawing effect of the nitro group, the Soret band is shifted from 413 nm for TPCorrGe(OCH_3) to 428 nm for (3-NO_2)TPCorrGe(OCH_3) and then to 432 nm for (3,17-NO_2)$_2$TPCorrGe(OCH_3). The Q-band of the compound is shifted from 589 in the absence of a nitro group to 607 nm for the mononitro corrole and then to 628 nm upon the addition of a second nitro group to give the dinitro corrole.

The Soret and visible bands decrease in intensity while a broad visible band between 650 and 900 nm grows in upon the first reduction or first oxidation of the mono- and dinitro derivatives in CH_2Cl_2 containing 0.1 M TBAP (Figures 9 and Figure S4, Supporting Information). This indicates that π-anion radicals and π cations are formed during the first reduction and first oxidation of these compounds, respectively.

Conclusions

We report here the preparation of β-nitro substituted Ge(IV) triphenylcorrolates, obtained by reaction of the starting corrole complex with nitrate salts/Ac_2O/AcOH. This is the first example of β-nitration of triphenylcorrole derivatives carried out with electrophilic reagents. Depending on the reaction conditions, it is possible to obtain mono- or bis-nitro Ge(IV) corrolates; in all cases, the reaction proceeds with high selectivity for substitution and only the 3- and 3,17-derivatives are obtained among the huge number of possible regioisomers. The β-nitro substituted Ge(IV) triphenylcorrolates are obtained from the substitution reaction as a mixture of the μ-oxo dimer and the corresponding hydroxide monomer. These species can be easily converted into the corresponding methoxide complex.

This article presents also the first study on electrochemistry and spectroelectrochemistry of the Ge(IV) corrolate complexes, elucidating the site of electron transfer and the influence of the nitro group. These β-nitro substituted complexes are important intermediates, and we are currently exploring these compounds for the preparation of more elaborated species based on corroles.

Acknowledgment. The support of the Robert A. Welch Foundation (K.M.K., Grant E-680) is gratefully acknowledged.

Supporting Information Available: Cyclic voltammograms, UV−visible spectroelectrochemical data, and a view of the molecular structure of [3,17-(NO_2)$_2$TPCorrGe]$_2$O along the Ge···Ge vector. CIF file of [3,17-(NO_2)$_2$TPCorrGe]$_2$O. This material is available free of charge via the Internet at http://pubs.acs.org.

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