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A Chiral meso-ABC-Corrolatochromium(V) Complex

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A chiral metallocorrole complex, oxo[5-(4-bromophenyl)-10-(pentafluorophenyl)-15-(2-thianaphthyl)corrolato]chromium(V) (**7**), was prepared and serves as the first example of an ABC-metallocorrole; meso substituents are of different electron-withdrawing capacity. An adaptation of a multistep protocol (D. T. Gryko) was made, followed by an aerobic oxidation using $Cr(CO)_6$ (Z. Gross). The X-ray crystal structure reveals the two enantiomers of **7**. Electron paramagnetic resonance spectroscopy (g_{iso} = 1.99) and cyclic voltammetry of **7** provide comparative data to that of the A_3[tris(pfp)cCr^VO] complex.

Corroles are a class of contracted porphyrin that inspire great interest as synthetic targets because of the preparation of metal complexes in which the metal generally rests stably in a higher valence state in the corrin-like macrocyclic skeleton.[1] The general ease of synthesis of *meso*-A_3-triarylcorroles has allowed a study of various synthetic metallooxo species as model systems.[2,3] These systems allow for insights into the catalytic cycles of peroxidases (e.g., horseradish peroxidase and monooxygenases such as cytochrome P-450) because high-valent oxometalloporphyrins are intermediates in these enzymatic systems. Model systems allow for a study of oxygen transfer from artificial oxidants such as iodosobenzene to model substrates such as simple saturated and unsaturated hydrocarbons. The nature of the metal–oxygen moiety is often influenced by peripheral (meso) substitutions and can be probed by electron paramagnetic resonance (EPR), such as in oxochromium(V) porphyrin complexes.[4]

Detailed and ground-breaking research in the area of oxo–metal species of corroles has been performed by Gross and co-workers[5] in which the tris(pentafluorophenyl)corrolatochromium system was studied in four formal oxidation states.[2a] The corrole-based Cr^VO/Cr^{III} cycle allows for aerobic oxidation of the substrate, in which the mild oxidative power of Cr^VO may be beneficial for catalytic processes in biological systems.[6] It should be noted that oxo–metal species are often obtained on the basis of A_3-triarylcorroles; variation of the meso substituents at the periphery of the corrole macrocyclic ring can significantly influence the properties of the final compounds.

There has been further interest in expanding corrole derivatization (D. T. Gryko), especially with regard to exploring materials chemistry, an exciting frontier that is still unfolding.[1c] In these applications, the substitutions can be quite different from what nature provides, such as in the construction of dyads,[7] and in efforts to target synthetic luminescent organic materials.[8] In terms of more complex ligands based on the meso-substituted systems, there has been interest in making the corrole version of the ABCD-porphyrin. Recently, Gryko and co-workers reported a synthesis involving a diacyl intermediate for corroles bearing three different *meso*-aryl substituents.[9]

Herein, the synthesis of a free-base corrole bearing three substituents was sought that, hence, would form a chiral complex upon formal oxometalation. Prior to this present study, the chemistry of *meso*-ABC-correlatometal complexes was completely undeveloped, perhaps because of the complicated synthetic procedure to obtain the free-base corrole. Aryl groups of different electron-withdrawing capacity can be incorporated (Scheme 1). The 4-bromophenyl,

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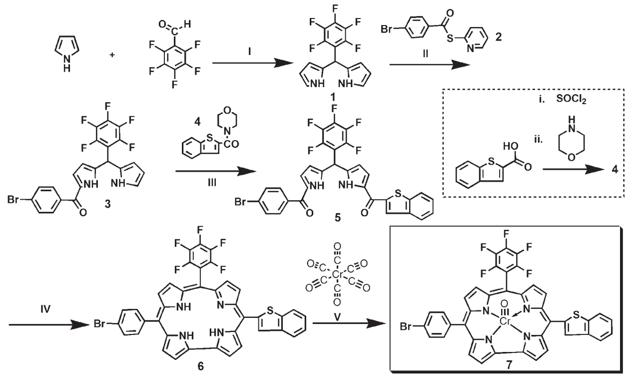
Scheme 1. (I) $InCl_3$-Catalyzed Condensation, (II) Monoacylation Using EtMgBr, (III) a Second Acylation Involving $POCl_3$, (IV) Free-Base Corrole Formation via TFA-Catalyzed Condensation and Radical Oxidative Cyclization by DDQ, and (V) Metalation via $Cr(CO)_6$ (Inset: Non-Grignard-Based Preparation of **5**)



2-thianaphthyl, and C_6F_5 groups were thus selected. The *p*-bromophenyl group may facilitate Pd coupling, 2-thianaphthyl allows for a clear oxidizable ligand site, proximal to an oxidizable metal ion,[10] and the C_6F_5 group lends increased ligand and complex stability. The incorporation of thiophenes in corrole meso positions has proven to be more difficult than that for porphyrins.[11] This laboratory has been involved in elucidating the chemistry of *meso*-thienyl substutition into various nonporphyrin polypyrrolic systems.[11b,12]

The ABC-corrole synthesis is based largely on the Gryko method.[9] Pentafluorophenyldipyrromethane was synthesized via an $InCl_3$-catalyzed reaction (Scheme 1, I) in high yield (~75%).[13] Monoacylation (Scheme 1, II)[14] of the dipyrromethane obtained was performed with *S*-2-pyridyl-4-bromobenzothionate[15] using a Grignard reagent (yield: ca. 85%). The incorporation of a second acyl group, however, was not successful via that methodology. It was thought that the steric bulk of thianaphthene, when approaching monoacyldipyrromethane, may be inhibiting the reactivity. This led us to a non-Grignard-based methodology[16] for obtaining the diacyl product from *N*-aroylmorpholine (Scheme 1, inset).

The free-base corrole was synthesized directly from the diacyldipyrromethane via trifluoroacetic acid (TFA)-catalyzed condensation and radical oxidative cyclization by dichlorodicyanoquinone (DDQ; Scheme 1, IV). Dry-column vacuum chromatography allowed for isolation of the red fluorescent corrole fraction. Purification was attempted from recrystallization of a CH_2Cl_2/hexane mixture, which afforded a residue that gave a single dark-green spot (thin-layer chromatography assaying). MALDI-TOF mass spectral data featured a prominent peak that signaled the expected corrole (M^+): *m*/*z* 752.57 (calcd), 752.38 (obsd) (see the Supporting Information). The ^{1}H NMR spectrum, however, revealed an unknown impurity (aromatic resonances) that was ultimately not possible to remove and is probably a decomposition product of **6**, formed during either synthesis or later. The crude, free-base corrole was treated directly with $Cr(CO)_6$ to easily afford an enantiomeric mixture of **7**; Cr^VO derivatives are bright red and stable and thus are easily obtainable via benchtop chromatographic and recrystallization methods.

The compound crystallizes as dark-violet jewel-like prisms out of CH_2Cl_2/hexane (1:2 by volume) into the monoclinic centrosymmetric space group *C*2/*c*. The Cr atom is displaced more out of the N_4 plane (0.58 Å) than in previous examples[5] in adopting the distorted square-pyramidal structure (Cr−N bond lengths: 1.914−1.945 Å); the axial Cr=O bond length is 1.57 Å (Figure 1 and Table S3 in the Supporting Information). Unlike for the tris(pfp)cCr^VO compound,[5] only the domed conformer ($\angle N_1-Cr-N_3$ = 144°; $\angle N_2-Cr-N_4$ = 145°) is present here in the unit cell of **7**. The complex lacks any symmetry element, and the crystal is ultimately a racemic mixture containing closely packed enantiomers (Figure 2). The "planar chirality" of the complex is due to the presence of three different substituents in the corrole (i.e., no rotation axis) along with the axial oxo ligand that eliminates the reflection plane present prior to metalation. Two enantiomers originate from the upward and downward oxo ligation

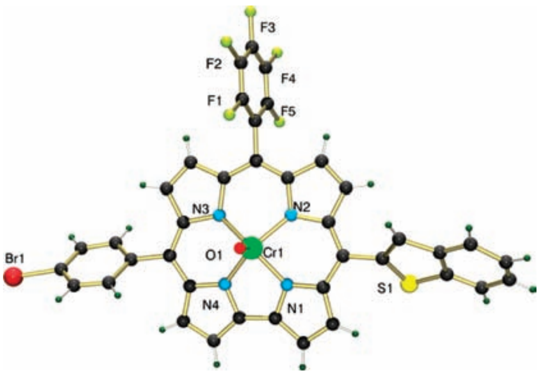


Figure 1. Molecular structure of **7**. Selected bond lengths (Å): N1−Cr1, 1.928(8); N2−Cr1, 1.936(7); N3−Cr1, 1.945(7); N4−Cr1, 1.914(8); O1−Cr1, 1.567(6).

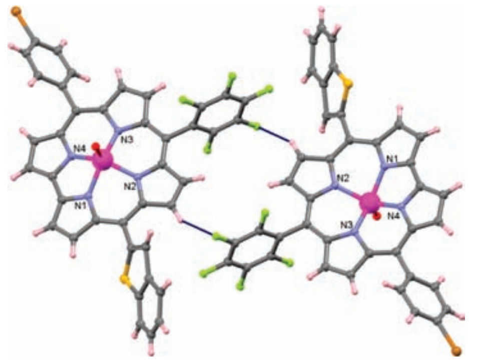


Figure 2. Two enantiomers in the crystal structure of **7** (the oxo ligand is upward and downward).

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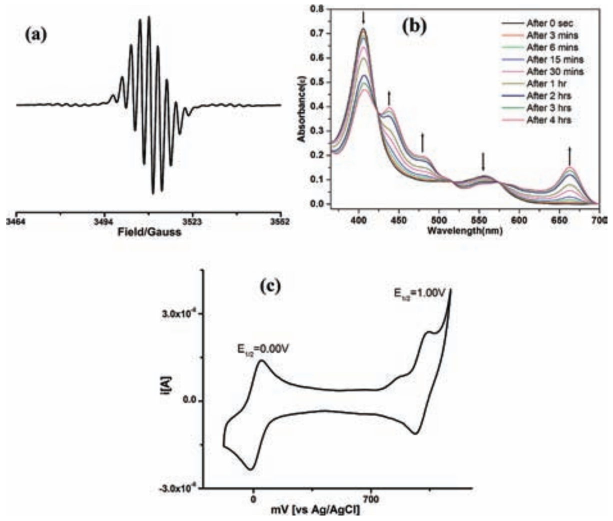

Figure 3. (a) EPR spectrum of **7**; CH_2Cl_2, 298 K. Microwave frequency, power, and modulation amplitude: 9.765 MHz, 5.0 mW, and 1.00 G, respectively. (b) UV−vis spectra of the catalytic conversion of PPh_3 to PPh_3O by **7** in CH_3CN (1 μM). (c) CV of **7**; 0.1 M tetrabutylammonium perchlorate/MeCN. Scan rate: 100 mV/s.

to the Cr center. The isolation of two enantiomers is quite difficult in this case, unless spontaneous resolution occurs during crystallization or a chiral auxiliary is employed.[17]

The EPR spectrum of **7** reveals a strong isotropic signal (g_0 = 1.989) due to ^{52}Cr (I = 0, 90.5%), resolved into nine lines via electron−nuclei hyperfine interaction with four equivalent ^{14}N nuclei (I = 1; Figure 3a). Satellite signals are attributed to the less abundant ^{53}Cr (I = $^3/_2$, 9.5%). A comparison of oxo-, nitrido-, and imidochromium(V) species is found in Table 1 and reveals a low spin density on the metal and a high spin density on the ligand. The σ-orbital electron density is donated from the pyrrole ultimately to the axial ligand.[4] In the case of the nitrido and imido complexes, the strong π-donating ability of the axial ligand negates the σ-donating effect (Table 1).[5,18] The A^{14}N coupling constant demonstrates that the degree of σ donation from the pyrrolic N atoms to the metal is greatest for the oxochromium(V) species. The A^{53}Cr hyperfine constant for **7** is less than that for tris(pfp)cCr^{V}O (1.59 vs 1.64 mT, respectively), which confirms the less π-bonding character of the Cr^{V}O moiety should be tris(pfp)cCr^{V}O.

Compound **7** allows for catalytic oxygenation of PPh_3 to PPh_3O in CH_3CN. The presence of a small amount of pyridine inhibits chromium reoxidation. UV−vis spectra revealed the growth of new peaks at 438 nm (Cr^{IV}) and ~476 and 662 nm (Cr^{III}) over time, along with gradual decreases of peaks at 406 and 556 nm (Cr^V) (Figure 3b). No further change was observed after 5 h, suggesting partial oxo transfer only, when considering the presence of bands assignable to Cr^V, Cr^{III}, and intermediate Cr^{IV} species. Thus, **7** is less catalytically active in this respect than A_3-(tris(pfp)cCr^{V}O).[6]

Table 1. EPR Parameters and Redox Potentials (V) vs Ag/AgCl for the Chromium(V) Corrolate Complexes

complex	g_{iso}	A^{53}Cr/ mT	A^{14}N/ mT	$E_{1/2}$(ligand/ ligand$^{\bullet+}$)	$E_{1/2}$(Cr^V/ Cr^{IV})
7	1.989	1.59	0.30	1.00	0.00
tris(pfp)cCr^{V}O[5]	1.986	1.64	0.30	1.25	0.11
tris(pfp)cCr^{V}N[18a]		2.67	0.27		
tris(pfp)cCr^V(NAr)[18b]	1.987	2.18	0.31	1.29	−0.13
tris(pfp)cCr^V(NMes)[18b]	1.985	2.18	0.31	1.31	−0.47

Cyclic voltammetric (CV) measurements revealed slight changes between A_3-(tris(pfp)cCr^{V}O) and **7**. The Cr^{5+}/Cr^{4+} redox couple for tris(pfp)cCr^{V}O and **7** has values of 0.11 and 0.00 V (vs Ag/AgCl), respectively,[5] revealing a significantly less positive redox potential for **7**. This is in accordance with the observed less favorable O-atom transfer to PPh_3 in the case of **7**. Furthermore, the *ligand*-based redox couple (ligand/ligand$^{\bullet+}$: 1.25 and 1.00 V, respectively) is also consistent with a lesser electron-withdrawing effect than that when more C_6F_5 groups are present. Thus, it is more difficult to reduce **7**, with its C_8H_5S/4-BrC_6H_4 groups, than it is to reduce tris(pfp)cCr^{V}O.

In conclusion, we have successfully synthesized oxo [5-(4-bromophenyl)-10-(pentafluorophenyl)-15-(2-thianaphthyl)corrolato]chromium(V), which is, to our knowledge, the *first* example of a *meso*-ABC-metallocorrole. The multistep synthesis involved three distinct incipient aryl groups with different electron-donating capacities. This chiral complex has been principally characterized by X-ray diffraction, EPR spectroscopy, and CV. In the X-ray structure, only the domed form is present, and a large N_4 plane displacement is apparent (0.58 Å). The EPR spectrum is consistent with a Cr^V center and bears satellite peaks. The CV data show the extent of a lowered electron-withdrawing capacity, manifested in the lowered performance of PPh_3 oxidation.

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Supporting Information Available: Details of syntheses, all types of NMR spectra related to this work, UV−vis, crystal data collection and refinements in PDF and CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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