Society, for the support of this research.

Registry No. *cis*-Pt(ethylene)(gly)Cl, 80081-27-2; *cis*-Pt(allyl alcohol)(gly)Cl, 80041-73-2; *cis*-Pt(allylsulfonate)(gly)Cl, 80041-74-3; *trans*-Pt(ethylene)(gly)Cl, 31902-31-5; *trans*-Pt(allyl alcohol)(gly)Cl, 80081-28-3; *trans*-Pt(allylsulfonate)(gly)Cl, 80081-29-4; *cis*-Pt(ethylene)(ala)Cl, 32661-13-5; *cis*-Pt(allyl alcohol)(ala)Cl, 80041-75-4; *cis*-Pt(allylsulfonate)(ala)Cl, 80041-76-5; *trans*-Pt(ethylene)(ala)Cl, 32680-87-8; *trans*-Pt(allyl alcohol)(ala)Cl, 80081-30-7; *trans*-Pt(allylsulfonate)(ala)Cl, 80081-31-8; *cis*-Pt(ethylene)(aba)Cl, 80041-77-6; *cis*-Pt(allyl alcohol)(aba)Cl, 80041-78-7; *cis*-Pt(allylsulfonate)(aba)Cl, 80041-79-8; *trans*-Pt(ethylene)(aba)Cl, 80081-32-9; *trans*-Pt(allyl alcohol)(aba)Cl, 80081-33-0; *trans*-Pt(allylsulfonate)(aba)Cl, 80081-34-1; Pt(ethylene)Cl_3^-, 12275-00-2; Pt(Me_2SO)Cl_3^-, 60881-14-3; *cis*-Pt(Me_2SO)(gly)Cl, 60383-64-4; *trans*-Pt(Me_2SO)(gly)Cl, 60338-47-8; Pt(gly)Cl_2^-, 24653-14-3.

Contribution from the Department of Chemistry,
University of South Carolina, Columbia, South Carolina 29208

Poly(pyrazolyl)borate Complexes of Zirconium(IV)

D. L. Reger* and M. E. Tarquini

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The organometallic chemistry of complexes of the second- and third-row transition metals to the left of the periodic table has been one of the most exciting and fast developing areas of inorganic chemistry. Complexes showing new reactivity patterns with small molecules,[1] containing new types of interesting ligands,[2] and possessing great potential usefulness in organic synthesis[3] have all been developed. In a majority of this chemistry, cyclopentadienylmetal halides are the starting materials. It seemed to us that the development of alternative metal halide starting materials containing ligands other than cyclopentadienyl rings could lead to new and interesting chemical transformations. Specifically, it was decided to prepare a new family of poly(pyrazolyl)borate metal halide complexes of zirconium, niobium, and tantalum. Our initial goal is to synthesize and investigate the reactivity of complexes of the general formula $[R_mB(pz)_{4-m}]_nMX_{p-n}$ (pz = pyrazolyl ring; $m = 1, 2$; $n = 1, 2$; M = Zr, $p = 4$, M = Nb, Ta, $p = 5$). Also of interest are complexes containing substituted pyrazolyl rings and complexes containing two different poly(pyrazolyl)borate ligands.

Although poly(pyrazolyl)borate complexes have been extensively studied with other transition metals,[4] only two reports of their zirconium, niobium, and tantalum complexes have appeared. Wilkinson et al.[5] have reported the complex $[H_2B(pz)_2]_2TaMe_3$. In addition, a short paper reporting the complexes (characterized only by ^1H NMR and Zr and Cl analytical figures) $[B(pz)_4]_2ZrX_2$ (X = Cl, Br) and $[B(pz)_4]_4Zr$ has appeared.[6]

This paper reports our initial results in this area. We have prepared a number of $[RB(pz)_3]ZrCl_3$ complexes and a methoxide derivative of one of these complexes. Also reported is the first isolation of the known ligand $[n\text{-BuB(pz)}_3]^-$ and the new ligand $[i\text{-PrB(pz)}_3]^-$.

Results and Discussion

At the onset of the investigation it was anticipated that ligands of the type $[RB(pz)_3]^-$ where R = alkyl would be the most desirable for this study in order to avoid complications arising from possible reactions of a BH group and, more importantly, to insure good solubility characteristics of the new complexes. To this end, the $Na[n\text{-BuB(pz)}_3]$ ligand salt had been prepared (reaction 1) but it had been used only in aqueous solution and not isolated.[7] We have now prepared and isolated in good yield both this ligand salt and $Na[i\text{-PrB(pz)}_3]$ utilizing the methodology of reaction 1.

$$\mathrm{B(OMe)_3} \xrightarrow[2.\ \mathrm{H_2SO_4/H_2O}]{1.\ n\text{-}\mathrm{BuMgBr}} n\text{-}\mathrm{BuB(OH)_2} \xrightarrow[2.\ \mathrm{Hpz}]{1.\ \mathrm{Na(pz)}} \mathrm{Na}[n\text{-}\mathrm{BuB(pz)_3}] \quad (1)$$

The reaction of either of these ligands or $[HB(3,5\text{-}Me_2pz)_3]^-$ with 2 equiv of $ZrCl_4$ yields the respective $[\text{ligand}]ZrCl_3$ complex in good yield. Stoichiometric reactions yielded inseparable mixtures of products. In the case of the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand, a series of reactions carried out between 1:1 and 1:2 molar ratios (ligand:metal) demonstrated that fully 2 equiv of $ZrCl_4$ are needed. Presumably, the extra equivalent of $ZrCl_4$ acts as a Lewis acid for the Cl^- being displaced. Note that in a very recent report it was stated that a 2:1 ratio of $ZrCl_4$ to TlCp was necessary in a new preparation of $CpZrCl_3$.[8]

The ^1H and ^{13}C NMR spectra of these new complexes show that the three pyrazolyl rings of the ligand are in equivalent environments (even at −80 °C for the $[HB(3,5\text{-}Me_2pz)_3]ZrCl_3$ complex) as expected for these pseudooctahedral complexes. All three compounds are soluble in CH_2Cl_2 and partially soluble (ca. 0.1 g/100 mL) in toluene. The $[HB(3,5\text{-}Me_2pz)_3]ZrCl_3$ complex is quite stable, decomposing in air only very slowly even in solution. It is also thermally stable as demonstrated by the fact that final purification (a step that presumably removes trace amounts of $ZrCl_4$) of this complex was effected by a 48-h Soxhlet extraction with benzene. The two $[RB(pz)_3]ZrCl_3$ complexes are much less stable, decomposing rapidly in air and also in refluxing benzene or pentane. Although less stable, these complexes are easily handled by standard Schlenk techniques. The higher stability of the $[HB(3,5\text{-}Me_2pz)_3]$ derivative is certainly not an unexpected result in view of the crystal structure data on $[HB(3,5\text{-}Me_2pz)_3]$ complexes, which show that the 3-Me substituents cause considerable steric crowding around the metal.[9]

In order to determine if this steric crowding would prevent possible reactivity, we prepared the methoxide derivative as shown in eq 2. This compound does not show fluxional behavior at 35 °C as has been observed in many poly(pyrazolyl)borate complexes.[10] Thus both ^1H and ^{13}C NMR spectra show a 2:1 ratio for each ring hydrogen and carbon atom, respectively, as expected for a static pseudooctahedral complex. These results also indicate that the ligand is indeed tridentate in this and, by extrapolation, in the three other new complexes reported above. The alternative explanation of a bidentate ligand could also possibly fit the NMR data but is unrea-

$$\mathrm{[HB(3,5\text{-}Me_2pz)_3]ZrCl_3 + NaOMe \xrightarrow{toluene} [HB(3,5\text{-}Me_2pz)_3]Zr(OMe)Cl_2 + NaCl} \quad (2)$$

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sonable in that one would expect the ligand to be fluxional in this case and would also expect similar NMR behavior for the other three complexes.

Currently, the organometallic chemistry of the starting materials described here is being pursued. We are encouraged by the ease of preparation, the solubility characteristics, and the stability of these new complexes.

Experimental Section

General Procedure. All operations were carried out under an atmosphere of prepurified nitrogen with use of standard Schlenk techniques. All solvents were dried, degassed, and distilled prior to their use. Infrared spectra were recorded on a Beckman Model IR4210 spectrometer. Proton NMR spectra were recorded on Varian Model EM360, EM 390, and IBM NR-80 spectrometers, and chemical shifts are reported in δ vs. Me_4Si. Carbon-13 NMR spectra were recorded on Varian CFT-20 and IBM NR-80 spectrometers with CH_2Cl_2, CD_2Cl_2, or $CDCl_3$ as the solvent and internal standard. Chemical shifts are reported in δ vs. Me_4Si, with the CH_2Cl_2 resonance assigned to be at 54.0 ppm, the CD_2Cl_2 resonance at 53.8 ppm, and the $CDCl_3$ resonance at 77.0 ppm. All carbon-13 spectra were run with ^1H decoupling, and all resonances may be assumed to be singlets. Carbon atoms bonded to boron were not observed. $K[HB(3,5\text{-}Me_2pz)_3]$ was prepared by the method of Trofimenko.[7] $ZrCl_4$ was used as obtained from Alfa Ventron. Alkylboronic acids were prepared by published methods.[11] Elemental analyses were performed by Robertson Laboratory and Galbraith Laboratory. It proved difficult to obtain high-quality analytical figures on the $RB(pz)_3$ (R = *n*-Bu, *i*-Pr) ligands and complexes. This problem has been reported by others.[4b] Note that attempts to crystallize these complexes (from mixtures of CH_2Cl_2, toluene, and/or hexane over a period of days and weeks at −20 °C) have failed, to date, and generally lead to sample degradation. Melting and decomposition points were determined in sealed capillaries and are uncorrected.

Sodium Isopropyltris(1-pyrazolyl)borate {Na[*i*-PrB(pz)$_3$]}. Freshly prepared isopropylboronic acid (4.16 g, 47.3 mmol) was placed in a 500-mL round-bottomed flask containing THF (50 mL) and a magnetic stirring bar. A sodium pyrazolide solution in THF (150 mL), prepared by adding a THF solution of pyrazole (3.50 g, 51.5 mmol) to a stirred NaH suspension (1.15 g, 47.9 mmol), was added slowly to the flask at room temperature by a cannula. Pyrazole (12.80 g, 188.2 mmol) in THF (100 mL) was added to the flask by a cannula. A reaction mixture was allowed to stir at room temperature overnight. Simple distillation of the reaction mixture yielded THF, H_2O, and finally pyrazole (bp 185 °C). After distillation of pyrazole, the temperature fell from 185 °C and the distillation was discontinued. The residue was allowed to cool to room temperature where it solidified. The crude solid was chipped out of the flask and finely ground with a mortar and pestle. The off-white solid was thoroughly washed with hexane (5 × 100 mL) under N_2. The solid was then dissolved in $CHCl_3$ (200 mL) and filtered through a medium-fritted disk. The filtrate was evaporated to dryness at room temperature under reduced pressure yielding a white solid, mp 151–154 °C (8.73 g, 67% based on isopropylboronic acid). Anal. Calcd for $C_{12}H_{16}N_6BNa$: C, 51.80; H, 5.76; N, 30.22. Found: C, 50.98; H, 5.91; N, 29.54. ^1H NMR spectrum ($CDCl_3$): δ 7.38, 7.17 (3, 3; d, d; J = 2.0 Hz, J = 1.6 Hz; 3-H, 5-H (pz)); 6.10 (3, t, J = 1.8 Hz, 4-H (pz)); 1.58 (1, m, CH); 0.71 (6, d, J = 6.4 Hz, CH_3). ^{13}C NMR spectrum (CH_2Cl_2): 141.0, 135.1 (3-C, 5-C (pz)); 104.7 (4-C (pz)); 19.5 ppm (CH_3).

Sodium *n*-Butyltris(1-pyrazolyl)borate {Na[*n*-BuB(pz)$_3$]}. This compound was prepared with use of the same procedure for Na[*n*-PrB(pz)$_3$] except that *n*-butylboronic acid was used, yielding a white solid, mp 125–128 °C (70%). Anal. Calcd for $C_{13}H_{18}N_6BNa$: C, 53.42; H, 6.16; N, 28.77. Found: C, 52.58; H, 6.14; N, 28.46. ^1H NMR spectrum ($CDCl_3$): δ 7.50, 7.24 (2, 2; d, d; J = 1.6 Hz, J = 1.4 Hz; 3-H, 5-H (pz)); 6.19 (3, t, J = 1.2 Hz, 4-H (pz)); 1.18 (4, m, CH_2); 0.81 (5, m, CH_2, CH_3). ^{13}C NMR spectrum (CH_2Cl_2): 141.0, 135.0 (3-C, 5-C (pz)); 104.8 (4-C (pz)); 27.8, 26.4 (CH_2); 14.1 ppm (CH_3).

[Hydrotris(3,5-dimethylpyrazolyl)borato]trichlorozirconium(IV) {[HB(3,5-Me$_2$pz)$_3$]ZrCl$_3$}. Zirconium (IV) chloride (8.32, 35.7 mmol) and potassium hydrotris(3,5-dimethylpyrazolyl)borate (6.00 g, 17.9 mmol) were combined in a 500-mL round-bottomed flask containing a magnetic stirring bar. After the flask was cooled to −78 °C, CH_2Cl_2 (300 mL), previously cooled to −78 °C, was added to the solids by a cannula. The reaction mixture was allowed to gradually warm up to 0 °C where it was stirred for 18 h. The cloudy, yellow solution was filtered with use of a medium-fritted disk, and the clear, yellow filtrate was evaporated to dryness at room temperature under reduced pressure (7.85 g, 89% based on the ligand). The product at this stage appears spectroscopically pure, but traces of metal chloride cause slightly high Cl and low C analytical figures (ca. 1%). The crude product was placed into a Soxhlet extraction apparatus and continuously extracted with benzene (75 mL) for 48 h. Filtration of the colorless benzene solution at room temperature yielded a white solid, mp 334 °C dec (4.94 g, 56% based on ligand). Note that the crude product was usually light yellow even though the pure product is white. Anal. Calcd for $C_{15}H_{22}N_6BCl_3Zr$: C, 36.41; H, 4.48; Cl, 21.50. Found: C, 36.74; H, 4.60; Cl, 21.21. ^1H NMR spectrum ($CDCl_3$): δ 5.84 (3, s, 4-H (pz)); 2.67, 2.39 (9, 9; s, s; 3-CH_3, 5-CH_3 (pz)). IR spectrum (cm^{-1} in CH_2Cl_2): ν(BH) 2560. ^{13}C NMR spectrum (−80 °C, CD_2Cl_2): 153.7, 147.1 (3-C, 5-C(pz)); 107.0 (4-C (pz)); 15.3, 12.8 ppm (3-CH_3, 5-CH_3 (pz)). The mass spectrum shows a multiple cluster with the highest peak at 494 as expected (from two ^{35}C and one ^{37}Cl) for the molecular ion.

[Hydrotris(3,5-dimethylpyrazolyl)borato]dichloromethoxyzirconium(IV) {[HB(3,5-Me$_2$pz)$_3$]Zr(OMe)Cl$_2$}. $[HB(3,5\text{-}Me_2pz)_3]ZrCl_3$ (0.50 g, 1.0 mmol) was placed in a 200-mL round-bottomed flask containing a magnetic stirring bar. Toluene (30 mL) was added via syringe, and the solution was cooled to −78 °C. Freshly prepared sodium methoxide (0.054 g, 1.0 mmol), prepared from sodium metal and methanol, was added slowly in a toluene suspension to the reaction. This mixture was allowed to stir at −78 °C for 1 h and warmed to room temperature. The cloudy white solution was filtered through a medium-fritted disk, and the clear, colorless filtrate was evaporated to dryness under reduced pressure at room temperature yielding a white solid, mp 289–292 °C (yield 0.41 g, 84%). Anal. Calcd for $C_{16}H_{25}N_6BCl_2OZr$: C, 39.12; H, 4.90; N, 17.13; Cl, 14.48. Found: C, 39.39; H, 5.15; N, 16.92; Cl, 14.21. ^1H NMR spectrum ($CDCl_3$): δ 5.74 (3, s, 4-H (pz)); 4.09 (3, s, OCH_3); 2.64, 2.49, 2.33 (3, 6, 9; s, s, s; 3-CH_3, 5-CH_3 (pz)). IR spectrum (cm^{-1} in CH_2Cl_2): ν(BH) 2555. ^{13}C NMR spectrum (in $CDCl_3$ the pz rings are nonequivalent in this compound and are labeled A and B; the ratio A:B is 2 to 1): 153.9 (B), 152.5 (A), 145.7 (A), 141.0 (B) (3-C, 5-C (pz)); 107.3 (B), 106.8 (A) (4-pz); 62.7 (OCH_3); 15.3 (B), 14.1 (A), 12.7 (A + B) ppm (CH_3 (pz)). The mass spectrum shows a multiple cluster (appropriate for an ion containing two Cl atoms) with highest peak at 488 (M^+).

[*n*-Butyltris(1-pyrazolyl)borato]trichlorozirconium(IV) {[*n*-BuB(pz)$_3$]ZrCl$_3$}. Zirconium(IV) chloride (2.39 g, 10.3 mmol) was placed in a 250-mL round-bottomed flask containing a magnetic stirring bar. The flask was cooled to −78 °C and cold (−78 °C) CH_2Cl_2 (50 mL) was added by a cannula. Na[*n*-BuB(pz)$_3$] (1.50 g, 5.14 mmol) was added slowly to the reaction flask in a CH_2Cl_2 (50 mL) solution at −78 °C. The reaction was allowed to stir for 2 h at −78 °C and then overnight at 0 °C. The cloudy white solution was filtered through a medium-fritted disk, and the filtrate was evaporated to dryness at room temperature under reduced pressure, yielding a white solid, mp 217–221 °C dec (yield 2.21 g, 92% base on ligand). Anal. Calcd for $C_{13}H_{18}N_6BCl_3Zr$: C, 33.46; H, 3.89; N, 18.00; Cl, 22.79. Found: C, 33.62; H, 4.40; N, 17.09; Cl, 21.06. ^1H NMR spectrum ($CDCl_3$): δ 8.07, 7.68 (3, 3; d, d; J = 2.0 Hz, J = 2.4 Hz; 3-H, 5-H (pz)); 6.23 (3, t, J = 2.0 Hz, 4-H (pz)); 1.6, 1.1 (9, m, *n*-Bu). ^{13}C NMR spectrum (CH_2Cl_2): 144.7, 135.3 (3-C, 5-C (pz)); 105.5 (4-C (pz)); 27.5, 26.9 (CH_2); 14.0 ppm (CH_3). Mass spectrum: The high-resolution spectrum shows a weak molecular ion (M^+) cluster and an intense cluster for $M^+ - C_4H_9$ (loss of the *n*-butyl group). Calcd for $^{12}C_{13}{}^1H_{18}{}^{14}N_6{}^{11}B^{35}Cl_2{}^{37}Cl^{90}Zr$, $^{12}C_{13}{}^1H_{18}{}^{14}N_6{}^{11}B^{35}Cl_3{}^{90}Zr$, $^{12}C_{13}{}^1H_{18}{}^{14}N_6{}^{11}B^{35}C_2{}^{37}Cl^{92}Zr$: 465.9769, 463.9798, 467.9768. Found: 465.9768, 463.9776, 467.9750.

[Isopropyltris(1-pyrazolyl)borato]trichlorozirconium(IV) {[*i*-PrB(pz)$_3$]ZrCl$_3$}. This compound was prepared as described for [(*n*-BuB(pz)$_3$)ZrCl$_3$] with Na[*i*-PrB(Pz)$_3$] in place of Na[*n*-BuB(pz)$_3$], mp 175–180 °C (yield 90%). Anal. Calcd for $C_{12}H_{16}N_6BCl_3Zr$: C, 31.83; H, 3.54; N, 18.56; Cl, 23.53. Found: C, 30.72, H, 3.75; N, 17.65; Cl, 23.26. ^1H NMR spectrum ($CDCl_3$): δ 8.09, 7.79 (3, 3; d, d; J = 2.0 Hz, J = 2.6 Hz; 3-H, 5-H (pz)); 6.24 (3, t, J = 2.6 Hz, 4-H (pz)); 2.0 (1, m, CH); 1.48 (6, d, J = 5.4 Hz, CH_3). ^{13}C NMR spectrum (CH_2Cl_2): 144.6, 136.1 (3-C, 5-C (pz)); 105.5 (4-C (pz));

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20.3 ppm (CH_3). Mass spectrum: The low-resolution spectrum shows a weak molecular ion cluster and an intense cluster at molecular ion $- C_3H_7$ (loss of isopropyl group). The high-resolution spectrum did not read out the molecular ion but did identify the $M^+ - C_3H_7$ cluster. Calcd for $^{12}C_9{}^1H_9{}^{14}N_6{}^{11}B^{35}Cl_2{}^{37}Cl^{90}Zr$, $^{12}C_9{}^1H_9{}^{14}N_6{}^{11}B^{35}Cl_3{}^{90}Zr$, $^{12}C_9{}^1H_9{}^{14}N_6{}^{10}B^{35}Cl_3{}^{90}Zr$, $^{12}C_9{}^1H_9{}^{14}N_6{}^{11}B^{35}Cl_2{}^{37}Cl^{92}Zr$: 408.9098, 406.9094, 405.9133, 410.9066. Found: 408.9083, 406.9097, 405.9134, 410.9076.

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Registry No. [HB(3,5-$Me_2pz)_3]ZrCl_3$, 80041-67-4; [HB(3,5-$Me_2pz)_3]Zr(OMe)Cl_2$, 80041-68-5; [*n*-$BuB(pz)_3]ZrCl_3$, 80041-69-6; [*i*-$PrB(pz)_3]ZrCl_3$, 80041-70-9; Na[*i*-$PrB(pz)_3$], 80041-71-0; Na[*n*-$BuB(pz)_3$], 80041-72-1; isopropylboronic acid, 80041-89-0; *n*-butylboronic acid, 4426-47-5; pyrazole, 288-13-1.

Contribution from the Institut für Anorganische Chemie,
Technische Hochschule Darmstadt,
D-6100 Darmstadt, Federal Republic of Germany, and
Physiologisch-chemisches Institut, Universität des Saarlandes,
D-6650 Homburg, Federal Republic of Germany

Oxochromium(IV) Porphyrins and Their Relationship to Heme Proteins

J. W. Buchler,* K. L. Lay, L. Castle, and V. Ullrich

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Recent evidence indicates the occurrence of ferryl porphyrin systems (oxoiron(IV) porphyrins) and oxoiron(V) porphyrins at the active sites of peroxidases[1] and cytochrome P 450,[2] respectively. As free oxoiron(IV) porphyrins themselves are unstable above −30 °C[3] and hence are only studied in solution,[4,5] other oxometal tetrapyrroles such as those of chromium[6-9] and manganese[10-13] are under investigation with a view to mimicking reactions of the active heme proteins mentioned. The model complexes can be obtained from their reduced counterparts by autoxidation or by oxidation with hypochlorite or iodosylbenzene. Thus, a chromium(V) corrole, CrO(OAC),[9,14] and a chromium(IV) phthalocyanine, CrO(Pc), have each been obtained as pure solids while a chromium(V) porphyrin of the presumed composition CrO(Cl)(TPP) has been investigated in solution.[6] For complexes with manganese, MnO(X)(TPP)·PhI (X unspecified, complex containing iodobenzene) has been obtained as a solid at −40 °C[12] and MnO(TPP) has been investigated by field ion desorption mass spectroscopy.[13]

We report here the preparation, isolation, and spectral characterization of the oxochromium(IV) porphyrins CrO(TTP) and CrO(OEP).[14] This work was undertaken as a continuation of our studies of oxo transition-metal porphyrins containing Ti^{IV}, V^{IV}, Mo^{IV}, Mo^{V}, W^{V}, Re^{V}, and Os^{VI}.[15] The reactivity of the oxochromium(IV) complexes toward alcohols and alkanes as typical substrates of peroxidases and cytochrome P 450,[1,16] respectively, has also been examined. First results are presented as follows.

While this note was in preparation, J.W.B. was informed that CrO(TPP) and CrO(TTP) with congruent properties have been obtained independently by Groves and co-workers[17a] during their current work on CrO(Cl)(TPP). Shortly thereafter, a paper of West and co-workers appeared describing a different synthesis and the X-ray structure determination of CrO(TPP).[17b]

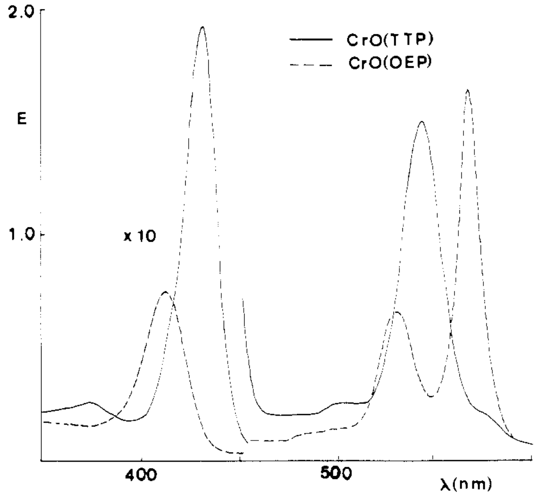

Figure 1. Optical absorption spectra of CrO(TTP) (—) and CrO(OEP) (---) in toluene. (The Soret bands are reduced by factors of 0.1.)

Experimental Section

Oxidation of Hydroxochromium(III) Porphyrins with Sodium Hypochlorite. (a) Preparation of Oxo(tetra-*p*-tolylporphinato)chromium(IV), CrO(TTP).[14] $Cr(OH)(TPP)\cdot 2H_2O$[18-20] (152 mg, 0.2 mmol) in 100 mL of $CH_2Cl_2/EtOH$ (98:2) was stirred with 1 mL of 2 M aqueous NaOH and 5 mL of aqueous NaOCl (13% active chlorine) until the color changed from violet-green to red. After the solution was washed with 2 M NaOH and taken to dryness in vacuo,

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* To whom correspondence should be addressed at the Technische Hochschule Darmstadt.

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[14] Abbreviations used: $(OAC)^{3-}$, octaalkylcorrole trianion; $(Pc)^{2-}$, phthalocyaninate dianion; $(TPP)^{2-}$ *meso*-tetraphenylporphinate dianion; $(TTP)^{2-}$, *meso*-tetra-*p*-tolylporphinate dianion; $(OEP)^{2-}$, octaethylporphinate dianion; Ph, C_6H_5; Et, C_2H_5.

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