

Synthesis, Characterization, and Reactivity of Novel Organochromium(III) Porphyrin Complexes¹

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The preparations of the organometallic porphyrin complexes (TTP)CrR (TTP is the dianion of *meso*-tetra-*p*-tolylporphyrin; R is C₆H₅, C₆H₄^tBu-*p*, or CH₂SiMe₃) are described. The new compounds were synthesized by metathesis of (TTP)CrCl with the corresponding organolithium or Grignard reagent and characterized by ¹H NMR and electronic spectroscopies. The reactivity of (TTP)CrR toward molecular oxygen in CDCl₃ and C₆D₆ solutions was investigated. In the former solvent, the initially observed products were (TTP)Cr(O) and RD, while little or no reaction occurred in the latter solvent until BrCCl₃ was added. These results suggest that the reaction commences upon coordination of dioxygen, followed by homolysis of the Cr-C σ-bond with subsequent trapping of R· by solvent or BrCCl₃, respectively. The reactive properties of (TTP)CrR with heat, light, acid, I₂, and HgCl₂ are also reported.

Many metalloid and metal porphyrin complexes that contain axial σ-bonded alkyl ligands are known,³⁻⁵ particularly for central atoms from groups 8, 9, 13, and 14. By comparison, there is still a paucity of reports concerning the organometallic chemistry of porphyrin complexes of the more oxophilic metals of groups 3-7 and the lanthanides. Prior investigations of σ-bonded hydrocarbyl metalloporphyrin complexes for metals in these groups include those for Sc,⁶ Y,^{7,8} Ti,⁹ Zr,^{10,11} Mo,¹² and Lu.^{8,13}

In light of a recent resurgence in interest regarding the organometallic chemistry of chromium(III),^{16,17} we have undertaken the study of organochromium(III) porphyrins in order to compare trends in reactivity of the metal-to-carbon σ-bond for the approximately isostructural series of organotransition metal(III) porphyrin compounds from the first transition series. Herein, we report the preparation and characterization of novel Cr(III) hydrocarbyl porphyrin complexes of type (TTP)CrR,¹⁸ where R is C₆H₅, C₆H₄^tBu-*p*, or CH₂SiMe₃, as well as the cleavage of the Cr(III)-C bond by O₂.

Experimental Section

Materials and Methods. All manipulations were performed via standard Schlenk-type methods or in a nitrogen-filled Vacuum Atmospheres glovebox equipped with an efficient recirculating atmosphere purification system. Nitrogen and argon (Liquid Carbonic, prepurified) were purified further by passage through an oxygen and water removal column consisting of MnO supported on silica. Toluene, pentane, and heptane, diethyl ether, and THF were purified by standard methods¹⁹ and freshly distilled from sodium benzophenone ketyl under nitrogen prior to use. C₆D₆ was dried over sodium, CDCl₃ was dried over 4-Å molecular sieves, and pyridine was dried over KOH. All were deoxygenated by three freeze-pump-thaw cycles and distilled under nitrogen. For the NMR scale experiments, CDCl₃ was additionally distilled from K₂CO₃ in the dark, in order to remove acidic impurities. Dioxygen was passed through a column of CaCl₂ and then through a dry ice/acetone trap to remove traces of water.

¹H NMR spectra were obtained on a Varian XL-300 spectrometer (299.943 MHz) at 25.0 ± 0.5 °C and referenced to (CH₃)₄-Si. Electronic spectra were recorded on either a Varian DMS 80 or Shimadzu UV-160 spectrophotometer. The liquid secondary ion mass spectrum (LSIMS) of (TTP)Cr(C₆H₄^tBu-*p*) was obtained at the Mass Spectrometry Facility at the Massachusetts Institute of Technology. The sample was dissolved in benzene through which argon had been bubbled for 5 min before use. A sulfolane matrix was applied to the fast atom bombardment (FAB) probe and degassed in a vacuum chamber before the sample solution was mixed with it. The spectrum was measured using the first two sectors (MS-1) of a JEOL HX110/HX110 tandem mass spectrometer, operating at 10 kV accelerating voltage, with 19 kV postacceleration at the detector. Resolution was 1:1000, and the primary beam was 15 keV Cs⁺ ions. Elemental analyses were determined at Galbraith Laboratories, Inc. (Knoxville, TN).

H₂TTP^{20,21} and (TPP)CrCl^{22,23} were prepared and purified according to literature procedures. (TTP)CrCl had spectral characteristics that were in close agreement with literature values.

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(18) Abbreviations: TTP is the dianion of *meso*-tetra-*p*-tolylporphyrin; TPP is the dianion of *meso*-tetraphenylporphyrin; OEP is the dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin.

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Vis (toluene): λ_{\max} 605, 566, 525, 450, 397 nm; (lit. vis (benzene)²²⁻²⁴: λ_{\max} 606, 566, 525, 450, 398 nm). ¹H NMR (CDCl₃): δ 7.2 (br s, tolyl *m*-H), 2.3 (br s, tolyl CH₃) (lit. ¹H NMR (CDCl₃):²⁴ δ 7.5–8.0, 2.34). C₆H₅Li (solution in cyclohexane/diethyl ether) and *p*-¹BuC₆H₄MgBr and Me₃SiCH₂MgCl (solutions in diethyl ether) were purchased from Aldrich.

Preparation of (TTP)CrR. A general preparation for (TTP)CrR is provided here. (TTP)CrCl (0.50 g, 0.66 mmol) was heated in vacuo at 100 °C overnight in order to drive off residual traces of HCl and water. The next day, the starting complex was suspended in toluene (30 mL) under nitrogen, the suspension was cooled to -78 °C, and a solution containing 1.3 times molar excess (0.86 mmol) of RLi (R = C₆H₅) or RMgX (R = C₆H₄^{*i*}Bu-*p*, X = Br; R = CH₂SiMe₃, X = Cl) was added (vide supra for corresponding solvents). The reaction mixture was protected from light and allowed to warm to room temperature. Small aliquots were withdrawn from time to time and the visible spectrum recorded in toluene. After 2 days, all starting material was consumed as demonstrated by the disappearance of the (TTP)CrCl bands at 605 and 450 nm. The solution was rapidly filtered through a plug (1.0-cm diameter, 0.5-cm length) of basic alumina (EM Science Aluminum oxide 90, basic, activity II-III, 70–230 mesh) in the dark. The alumina was washed with toluene (7 mL), the combined filtrates were reduced in volume to 10 mL, and pentane (20 mL) was carefully added. The solvent layers were allowed to mix slowly overnight, and subsequent cooling of the mixture to -40 °C provided a purple powder, which was filtered out and dried (typical yields were 30–50%).

We encountered difficulties in obtaining satisfactory elemental analyses for the new compounds, since they rather tenaciously held onto occluded solvent molecules, especially toluene. After considerable effort, we were able to obtain an acceptable analysis for solvent-free (TTP)Cr(C₆H₅). Anal. Calcd for C₅₄H₄₁N₄Cr: C, 81.28; H, 5.18; N, 7.02. Found: C, 80.82; H, 5.41; N, 6.70. For (TTP)Cr(C₆H₄^{*i*}Bu-*p*), the best analysis suggested that the sample was a 0.75 toluene solvate. Anal. Calcd for C₅₈H₄₉N₄Cr·0.75C₇H₈: C, 82.29; H, 6.01; N, 6.07. Found: C, 82.29; H, 6.14; N, 5.70. In order to confirm the identity of this complex as (TTP)Cr(C₆H₄^{*i*}Bu-*p*), the fast atom bombardment (FAB) liquid secondary ion mass spectrum of it was obtained. Three main manifolds are evident at higher *m/e* values in the mass spectrum, with maxima at *m/e* 720.2, 736.1, and 853.2. For the very air-sensitive (TTP)Cr(CH₂SiMe₃), a reasonably close analysis suggested that the sample was a 0.40 toluene solvate. Anal. Calcd for C₅₂H₄₇N₄SiCr·0.40C₇H₈: C, 77.90; H, 5.99; N, 6.63. Found: C, 77.97; H, 6.06; N, 6.19.

The visible spectra for all three new complexes were identical within experimental error. Vis (toluene): λ_{\max} 578 (sh), 543, 435, 392 nm. The ¹H NMR spectral data for (TTP)CrR at 25 °C follow. In CDCl₃, only the resonances for the relatively narrow *m*-H and methyl groups of the tolyl moiety are reported. For R = C₆H₅, ¹H NMR (CDCl₃): δ 6.90 (br s, tolyl *m*-H), 1.92 (br s, tolyl CH₃). ¹H NMR (C₆D₆): δ 10.4 (very br s, tolyl *o*-H), 6.70 (br s, tolyl *m*-H), 1.65 (br s, tolyl CH₃), -20.3 (very br s, pyrrolic H). For R = C₆H₄^{*i*}Bu-*p*, ¹H NMR (CDCl₃): δ 6.90 (br s, tolyl *m*-H), 4.00 (br s, ¹Bu CH₃), 1.91 (br s, tolyl CH₃). ¹H NMR (C₆D₆): δ 10.3 (very br s, tolyl *o*-H), 6.69 (br s, tolyl *m*-H), 3.90 (br s, ¹Bu CH₃), 1.64 (br s, tolyl CH₃), -21.3 (very br s, pyrrolic H). For R = CH₂SiMe₃, ¹H NMR (CDCl₃): δ 6.96 (br s, tolyl *m*-H), 1.93 (br s, tolyl CH₃). ¹H NMR (C₆D₆): δ 10.5 (very br s, tolyl *o*-H), 6.72 (br s, tolyl *m*-H), 1.67 (br s, tolyl CH₃), -9.14 (br s, SiMe₃), -19.1 (very br s, pyrrolic H). Sharp signals for occluded toluene occurred at δ 2.3 and 2.1 in CDCl₃ and C₆D₆, respectively, while occluded heptane was sometimes observed in the range δ 0.85–1.35.

Reactions of (TTP)Cr(C₆H₅) with O₂ in CDCl₃. (TTP)Cr(C₆H₅) (4.6 mg, 5.8 μ mol) was dissolved in CDCl₃ (0.50 mL) in an NMR tube that was protected from light, under an atmosphere of nitrogen, and closed with a serum cap. O₂ (0.14 mL, 5.8 μ mol) was added via syringe and the tube shaken for 10

s, after which it was immediately cooled in a dry ice/acetone bath. The tube was warmed to -45 °C, and the ¹H NMR spectrum was taken. The spectrum showed that all of the starting material was converted into the diamagnetic (TTP)Cr(O) and C₆H₅D (vide infra). ¹H NMR (CDCl₃, -45 °C): δ 9.00 (s, 8 H, pyrrolic-H), 8.07 (d, 4 H, tolyl *o*-H), 7.95 (d, 4 H, tolyl *o*-H), 7.47 (m, 8 H, tolyl *m*-H), 7.13 (s, benzene), 2.61 (s, 12 H, tolyl CH₃) (lit. values in ref 25).

The above reaction mixture was allowed to stand at room temperature for 1 day (still protected from light). The ¹H NMR spectrum at this time displayed line widths that indicated that (TTP)Cr(O) had decomposed to a Cr(III) complex, (TTP)CrX (X = Cl or OH). At this point, the tube was opened to air and all volatiles were distilled and collected. GC/MS analysis of the volatiles revealed the presence of C₆H₅D (*m/e* 79.1), along with some C₆H₆ (*m/e* 78.1) in the ratio of 3.25:1. After the GC/MS experiment, addition of a small amount of benzene to the volatiles demonstrated an attendant increase in intensity for the purported benzene singlet resonance. Chlorobenzene, phenol, and biphenyl all give complex ¹H NMR signals under identical sampling conditions.

In another experiment, (TTP)Cr(C₆H₅) was allowed to react with O₂ at -45 °C. ¹H NMR spectra were recorded at -45, -25, -15, 15, 35, and 45 °C. Identical coalescence behavior to that previously reported^{25a} for (TTP)Cr(O) was observed, thus further confirming the spectral assignment of the diamagnetic metalloporphyrin product.

Experiments were also performed in which at least 1 equiv of pyridine was added to (TTP)Cr(C₆H₅) prior to the addition of O₂. The ¹H NMR spectrum after addition of the pyridine had new broad resonances at δ 7.20 (tolyl *m*-H), 3.88 (presumably due to pyridine), and 2.14 (tolyl CH₃), as well as δ 7.14 for C₆H₅D. After addition of 1.2 equiv of O₂, no further reaction took place. In fact, the ¹H NMR spectrum remained unchanged over the course of several days. The metal-containing product appeared to be a Cr(III) porphyrin, on the basis of the chemical shifts and line widths of the resonances in the ¹H NMR spectrum.²⁵ The stability of this complex toward dioxygen suggests that it is not the exceedingly air-sensitive dipyrindine adduct of (TTP)Cr^{II}.²⁷⁻²⁹ The identity of this complex is most likely the pyridine adduct of (TTP)CrCl, resulting from chloride abstraction from the solvent by the intermediate Cr(II) complex formed after Cr–C bond homolysis. Halide abstraction from alkyl halides, especially polyhaloalkanes, is reportedly a facile process for Cr(II) complexes.³⁰

Reactions of (TTP)Cr(C₆H₅) with O₂ in C₆D₆. (TTP)Cr(C₆H₅) (4.0 mg, 5.0 μ mol) was dissolved in C₆D₆ in an NMR tube protected against air and light. O₂ (0.15 mL, 6.2 μ mol) was added, and the mixture was monitored via ¹H NMR spectroscopy. Essentially no reaction was observed during a period of 1 day.

A similar experiment was executed, except that, before the admission of O₂, BrCCl₃ (0.50 μ L, 5.0 μ mol) was added. The ¹H NMR spectrum of the oxygenated mixture, recorded after 1 h, revealed the formation of (TTP)Cr(O), (TTP)CrX (X = halide or OH), and BrC₆H₅. ¹H NMR (C₆D₆): δ 9.24 (s, 8 H, pyrrolic-H (TTP)Cr(O)), 7.97 (d, 8 H, tolyl *o*-H), 6.6–7.4 (m, tolyl *m*-H (TTP)Cr(O) and BrC₆H₅ superimposed on broader manifold of tolyl *m*-H (TTP)CrX), 2.40 (s, 12 H, tolyl CH₃ (TTP)Cr(O)), 1.7 (br s, tolyl CH₃ (TTP)CrX) (lit. values in ref 31 for ¹H NMR of

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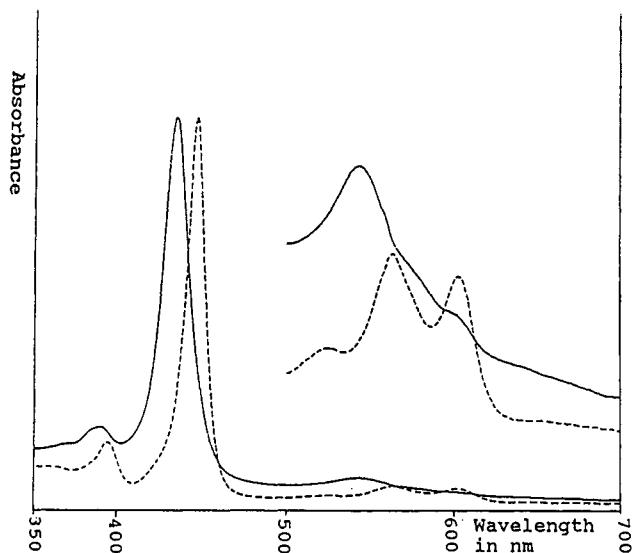


Figure 1. Electronic spectra of toluene solutions of (TTP)Cr(C₆H₅) (solid line) and (TTP)CrCl (dashed line).

(TTP)Cr(O) in C₆D₆). If larger amounts of BrCCl₃ were employed, a much faster formation of (TTP)Cr(O) was observed.

Reaction of (TTP)CrR (R = C₆H₄^tBu-*p*, CH₂SiMe₃) with O₂ in CDCl₃. The reaction of either (TTP)Cr(C₆H₄^tBu-*p*) or (TTP)Cr(CH₂SiMe₃) with O₂ in CDCl₃ was performed as for (TTP)Cr(C₆H₅) (vide supra). In each case, the formation of the corresponding hydrocarbon (*p*-^tBuC₆H₄D and CH₂DSiMe₃) and (TTP)Cr(O) was initially observed, followed by the subsequent decomposition of the chromyl species to (TTP)CrX (X = Cl or OH).

Results and Discussion

Preparation and Spectral Characterization of (TTP)CrR. When Cr(TTP)Cl is treated with a slight excess (1.3 equiv) of RLi (R = C₆H₅) or RMgX (R = C₆H₄^tBu-*p*, X = Br; R = CH₂SiMe₃, X = Cl) in THF, the green color of the original solution is slowly replaced by a deep reddish color. The extent of reaction is conveniently monitored spectrophotometrically by a shift in the Soret band from 450 to 435 nm and the disappearance of the absorption at 605 nm (see Figure 1 for R = C₆H₅). Workup of the reaction mixture by passage through a short plug of basic alumina, followed by recrystallization from toluene/pentane, provided deep red-brown (TTP)CrR in 30–50% optimized yield.

The new complexes are extremely sensitive to dioxygen in solutions containing radical scavengers (vide infra), although they are moderately stable in the solid state. The air sensitivity of the organochromium complexes (TTP)CrR, combined with their tendency to strongly retain solvent molecules in the solid state, led to difficulties in obtaining satisfactory elemental analyses of solvent-free complexes, except in the case of R = C₆H₅ (see Experimental Section). In retrospect, such problems are not surprising, since recent studies involving metalloporphyrin complexes have clearly demonstrated the propensity of these compounds for holding onto solvent molecules in the solid state.^{32–34}

In order to unequivocally establish the identity of the complex with R = C₆H₄^tBu-*p*, we resorted to FAB MS techniques. The liquid secondary ion mass spectrum of (TTP)Cr(C₆H₄^tBu-*p*) contains three main manifolds at higher *m/e* values. The peak centered at *m/e* 853.2 is attributable to the parent ion, [(TTP)Cr(C₆H₄^tBu-*p*)]⁺.³⁵ The largest manifold at *m/e* 720.2 can be assigned to loss of the aryl ligand to give [(TTP)Cr]⁺, while the small *m/e* 736.1 peak is almost certainly due to [(TTP)Cr(O)]⁺, formed via a decomposition of the organochromium complex by dioxygen in the sample solution (vide infra) prior to or upon introduction to the FAB probe.

The electronic spectrum of (TTP)Cr(C₆H₅) (Figure 1), as well as the other two organometallic complexes in this study, is somewhat less resolved in the 500–600-nm region than that for (TTP)CrCl. The Soret band is blue-shifted in the organochromium(III) compounds by 15 nm from that in (TTP)CrCl, possibly due to the increased σ -donor ability of the hydrocarbyl ligands relative to chloride. Similar changes are apparent in the electronic spectra of (TPP)FeCl₃³⁶ vs (P)Fe(C₆H₅) (P = TPP^{37–40} or TTP³⁸). It is interesting to note that while dilute solutions of (TTP)CrCl are green, dilute solutions of (TTP)CrR are orange-brown. The electronic spectra of chromium(III) porphyrins are quite complex to interpret,^{41,42} and we offer no quantitative explanation for this observation. Qualitatively, however, the color difference is probably attributable to overall stronger absorption in the green region and weaker absorption in the red region of the spectrum (Figure 1) by the organochromium(III) complexes.

The accuracies of magnetic susceptibility measurements by Evan's NMR method^{43,44} were hampered by the occlusion of variable quantities of solvent by the complexes. By approximating the amount of toluene and/or heptane occluded, we could estimate that μ_{eff} for the new compounds is in the range 3.3–4.0 μ_{B} , which is similar to previously reported values for Cr(III) porphyrins having three unpaired electrons.^{45–47} As such for an $S = 3/2$ ground state, we expected the likelihood of broad resonances and contact shifts in the ¹H NMR spectra of the complexes.²⁴

The ¹H NMR spectra of the new compounds were studied in CDCl₃ and more extensively in C₆D₆ due to their greater stability in the latter solvent. In CDCl₃ (25 °C), the spectra exhibit two relatively broad resonances (line width 40–150 Hz) attributable to the porphyrin ligand at ca. 1.90 and 6.90 ppm. These resonances can be assigned to *p*-CH₃ and *m*-H of the tolyl moiety by analogy to the assignments for (TTP)CrCl.²⁴ In C₆D₆ (25 °C), these

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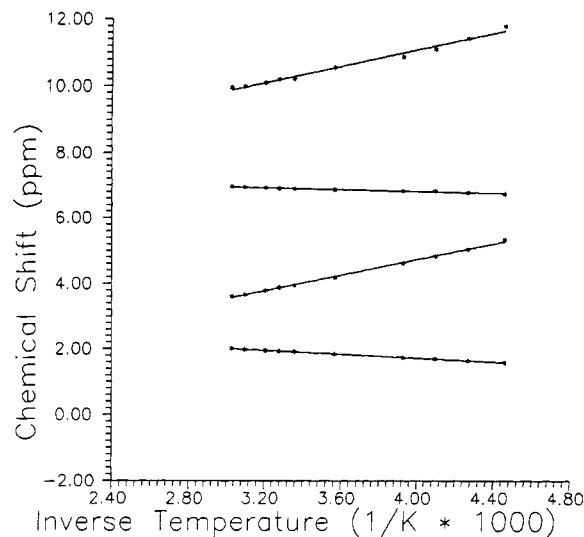


Figure 2. Curie plots for $(\text{TTP})\text{Cr}(\text{C}_6\text{H}_4^t\text{Bu-}p)$ in CDCl_3 solution. The temperature range is -48.8 to 57.0 °C. The linear regression lines have the following resonance assignments from top to bottom: tolyl *o*-H, tolyl *m*-H, $^t\text{Bu-CH}_3$ ($\text{C}_6\text{H}_4^t\text{Bu-}p$ group), and tolyl CH_3 . The pyrrolic H resonance was too broad at lower temperatures to accurately assess its chemical shift values. However, the changes in chemical shift for this resonance with change in temperature were consistent with its expected diamagnetic position.

resonances occur at ca. 1.65 and 6.70 ppm with comparable line widths. If a larger number of transients are collected in the latter solvent, then two considerably broader resonances are observed at ca. -19 to -21 ppm (line width 2000–3500 Hz) and 10.4 ppm (line width 400–1000 Hz). The former can be assigned to the pyrrolic-H,²⁶ while the latter would then be assigned to the *o*-H of the tolyl group. In addition, axial ligand resonances were observed in some cases. The $^t\text{Bu-CH}_3$ of the Cr-bound $\text{C}_6\text{H}_4^t\text{Bu-}p$ ligand resonates at 3.90 ppm (line width 150 Hz), while the methyl groups of the $\text{Cr-CH}_2\text{SiMe}_3$ functionality give rise to a peak at -9.1 ppm (line width 750 Hz).

The chemical shifts in the ^1H NMR spectra of the organochromium(III) porphyrin complexes are temperature dependent, as anticipated. A plot of the chemical shifts of the tolyl *o*-H, tolyl *m*-H, $^t\text{Bu-CH}_3$, and tolyl- CH_3 groups of $(\text{TTP})\text{Cr}(\text{C}_6\text{H}_4^t\text{Bu-}p)$ vs the inverse of the absolute temperature (Figure 2) shows that each resonance displays Curie behavior. The intercepts of the linear regression lines, which are the extrapolated shifts at infinite temperature, are 6.0 , 7.4 , 0.2 , and 2.8 ± 0.3 ppm for the above assignments, respectively. These values are close to the expected diamagnetic positions^{10,48,49} except for *o*-H. The latter discrepancy (ca. 2 ppm) may be due to the large line width of this resonance at lower temperatures and the attendant difficulty in ascertaining the exact peak position. If only higher temperature data are considered, then the extrapolated shift at infinite temperature for *o*-H is 8.0, in agreement with expectations from the literature.^{48,49}

Reaction of $(\text{TTP})\text{CrR}$ with Molecular Oxygen in Solution. Anaerobic solutions of $(\text{TTP})\text{CrC}_6\text{H}_5$ in dry CDCl_3 , which was distilled from K_2CO_3 , are indefinitely stable in the dark (Figure 3a); however, the introduction

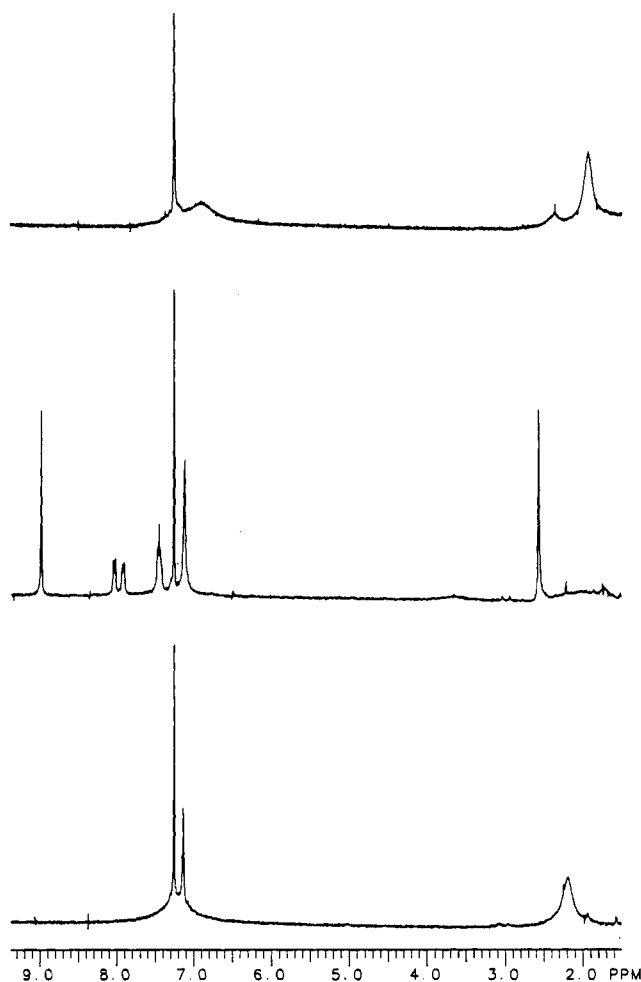


Figure 3. ^1H NMR spectra of $(\text{TTP})\text{Cr}(\text{C}_6\text{H}_5)$ and its reaction with O_2 in the dark in CDCl_3 solution: (a, top) before addition of O_2 , 25 °C; (b, middle) after addition of 1 equiv of O_2 , -45 °C; (c, bottom) after standing overnight, 25 °C.

of dioxygen under exclusion of light results in a relatively rapid reaction to give $(\text{TTP})\text{Cr}(\text{O})$ and $\text{C}_6\text{H}_5\text{D}$ (Figure 3b). Diamagnetic $(\text{TTP})\text{Cr}(\text{O})$ was identified by the characteristic chemical shifts and dynamic properties of its ^1H NMR spectrum.²⁵ $\text{C}_6\text{H}_5\text{D}$ was identified by GC/MS analysis and addition of benzene to the solution (see Experimental Section). No $\text{C}_6\text{H}_5\text{Cl}$, biphenyl, or oxygenated aromatic products could be detected in the spectral or chromatographic analyses. Under the reaction conditions, the chromyl porphyrin complex eventually is slowly converted to paramagnetic $(\text{TTP})\text{CrX}$ ($\text{X} = \text{Cl}$ or OH ; Figure 3c).⁵⁰ $(\text{TTP})\text{CrR}$ ($\text{R} = \text{C}_6\text{H}_4^t\text{Bu-}p$ or CH_2SiMe_3) reacted with dioxygen in an entirely analogous manner to give $(\text{TTP})\text{Cr}(\text{O})$ and the corresponding monodeuterated arene or alkane.

The exact mechanism of decomposition of $(\text{TTP})\text{CrR}$ by dioxygen in CDCl_3 is problematical at present; however, the following observations shed some light on possible reaction steps. The initial coordination of dioxygen at the vacant axial site trans to the hydrocarbyl ligand of the organochromium complex is suggested by the analogous cleavage of the Cr–C bond in CDCl_3 to give $\text{C}_6\text{H}_5\text{D}$ and a Cr(III) porphyrin product by the addition of dry pyridine, a good Lewis base that is known to coordinate well to chromium(III) porphyrin complexes (see Experimental

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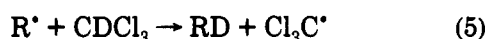
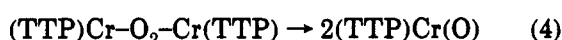
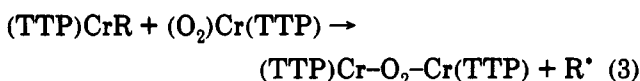
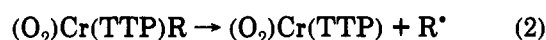
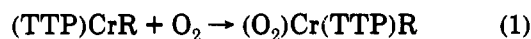
(50) We thank a reviewer for the suggestion that X may be a hydroxide ligand.

Section).^{23,51-54} Both putative coordination reactions were too rapid to detect adducts of the type $\text{LCr}(\text{TTP})(\text{C}_6\text{H}_5)$ ($\text{L} = \text{O}_2$ or pyridine), even at -45°C .

We speculate that the ensuing reaction steps to form $(\text{TTP})\text{Cr}(\text{O})$ and $\text{C}_6\text{H}_5\text{D}$ are radical in nature and intimately involve the CDCl_3 solvent. The formation of $\text{C}_6\text{H}_5\text{D}$ can be rationalized as the rapid extraction of D from solvent in the solvent cage by phenyl radicals, a known rapid process for phenyl^{55,56} or alkyl^{55,57,58} radicals and CHCl_3 . Further evidence for intervention of the solvent is provided by the ultimate formation of $(\text{TTP})\text{CrX}$ ($\text{X} = \text{Cl}$ or OH) as the final metalloporphyrin product. Chromyl porphyrin complexes are known to be relatively stable in dry, neutralized CHCl_3 or CH_2Cl_2 solution,^{25a,59,60} but possible formation of phosgene⁵⁵ and/or HCl from decomposition of CCl_3 radicals or slow oxidation of the solvent³¹ could likely lead to conversion of $(\text{TTP})\text{Cr}(\text{O})$ to either $(\text{TTP})\text{CrCl}$ or $(\text{TTP})\text{Cr}(\text{OH})$.

Somewhat surprisingly, $(\text{TTP})\text{Cr}(\text{C}_6\text{H}_5)$ reacts only very slowly, if at all, with dioxygen in C_6D_6 . However, when the good radical scavenger BrCCl_3 ^{55,61-63} is added to the solution, resonances for $(\text{TTP})\text{Cr}(\text{O})$, $(\text{TTP})\text{CrX}$ ($\text{X} = \text{halide}$ or OH), and $\text{C}_6\text{H}_5\text{Br}$ rapidly appear. These results can also be interpreted as arising from homolytic cleavage of the $\text{Cr}-\text{C}$ bond. Again, no biphenyl coupling product or oxygenated aromatic products could be detected.

Keeping the above observations in mind, we can propose the following mechanism for $\text{Cr}-\text{C}$ bond cleavage by dioxygen in CDCl_3 solution:



Initial coordination of molecular oxygen (eq 1), followed by rapid homolytic cleavage of the $\text{Cr}-\text{C}$ bond (eq 2), would give $(\text{O}_2)\text{Cr}(\text{TTP})$.⁶⁴ This molecule is formally a dioxygen adduct of a $\text{Cr}(\text{II})$ porphyrin; the chemistry of such complexes has been previously described.^{25b,29} We do not

believe that the homolytic cleavage occurs thermally without prior coordination of the dioxygen molecule (vide supra); $(\text{TTP})\text{CrR}$ complexes are stable in CDCl_3 solution in the dark in the absence of O_2 .

We hypothesize that $(\text{O}_2)\text{Cr}(\text{TTP})$ then quickly reacts with another molecule of $(\text{TTP})\text{CrR}$ (eq 3) to form a μ -peroxo-bridged dimer, followed by homolytic fission of the $\text{O}-\text{O}$ bond to give two molecules of the chromyl complex, $(\text{TTP})\text{Cr}(\text{O})$ (eq 4). Although steps 3 and 4 lack good precedence in chromium chemistry, they or similar reactions have been previously proposed to explain the oxidation of $\text{Cr}(\text{II})$ porphyrins by O_2 in solution^{25b} by analogy to well-established $\text{Fe}(\text{II})$ chemistry.⁶⁵ Under the reaction conditions, $(\text{TTP})\text{Cr}(\text{O})$ is then more slowly decomposed to $(\text{TTP})\text{CrCl}$, probably through the intervention of products derived from the Cl_3C radical (step 6).⁵⁵

Perhaps the most quarrelsome point in the proposed mechanism is the fate of the aryl or alkyl radicals generated. NMR and GC/MS analyses point to the formation of only monodeuterated arene or alkane, within detectable limits. We argue that the solvent, CDCl_3 , is acting as an efficient radical scavenger; that is, as fast as R^\bullet forms, it is intercepted by CDCl_3 (step 5). Since no coupling of R^\bullet radicals is observed, this interpretation assumes that R^\bullet is not readily diffusing out of the solvent cage. Incorporation of oxygen atoms into the organic products would not likely be expected if R is aryl, since it has previously been demonstrated that phenyl radicals do not show any tendency to react with molecular oxygen.^{66,67}

We can extend this argument to the case of C_6D_6 solutions of $(\text{TTP})\text{CrR}$, where essentially no reaction with dioxygen takes place until BrCCl_3 is added. In the absence of a good radical scavenger, we believe that rapid recombination of $(\text{O}_2)\text{Cr}(\text{TTP})$ with R^\bullet is likely occurring in C_6D_6 . Similar "kinetic" stability is observed for organocobalt(III) complexes, where radical scavengers can be employed to drive the homolytic cleavage reaction of the $\text{Co}-\text{C}$ bond to completion.^{68,69} Although reaction of $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ with R^\bullet is not diffusion-controlled in aqueous solutions,³⁰ it is perhaps sufficiently fast ($k \sim 10^8 \text{ M}^{-1} \text{ s}^{-1}$) in the relatively viscous aqueous solvent to account for our observations in the much less viscous C_6D_6 . Solvent viscosity has been demonstrated to play an important role in radical recombination processes of this type.⁷⁰

It is of interest to compare the reaction of molecular oxygen with $(\text{TTP})\text{CrR}$ to literature results involving the interaction of O_2 with other organometallic porphyrin complexes with central metal ions from the first transition series, including Ti, Fe, and Co. In the case of $(\text{P})\text{CoR}$ ^{71,72} and $(\text{P})\text{CoLR}$ ⁷² ($\text{P} = \text{TPP}, \text{OEP}$; $\text{R} = \text{CH}_3, \text{CH}_2\text{CH}_3, \text{CH}_2\text{C}_6\text{H}_5$; $\text{L} = \text{pyridine}, \text{P}(\text{C}_6\text{H}_5)_3$), the cleavage of the $\text{Co}-\text{C}$ bond requires the action of light. If the photolysis is carried out in either oxygen-saturated CHCl_3 /pyridine

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(95:5)⁷¹ or CH₂Cl₂,⁷² then insertion occurs to give isolable⁷² (P)Co(OOR) complexes.

The oxygen cleavage reactions of the Fe-C bond in organoiron porphyrin complexes, (TTP)FeR, have been the subjects of several elegant studies,⁷³⁻⁷⁷ through which a more complex picture has emerged. In toluene solutions of (TTP)FeR (R = alkyl or aryl) at temperatures at or below 25 °C, thermal insertion of O₂ into the Fe-C bond occurs to produce the intermediate (TTP)Fe(OOR).⁷⁴⁻⁷⁷ This compound decomposes by homolytic scission of the O-O bond to give the ferryl complex, (TTP)Fe(O), and RO•.^{73,74} The subsequent free radical chemistry depends upon the nature of R. If R is an alkyl group that has at least one α-hydrogen atom, then the ultimate products are (TTP)Fe-O-Fe(TTP) and an aldehyde or ketone.^{74,75} If R is an aryl moiety, then (TTP)Fe(OR) is the major product.⁷⁶ However, if (OEP)Fe(C₆H₅) is exposed to dioxygen in toluene at 80 °C, then the final products are (OEP)Fe-O-Fe(OEP) and biphenyl, which probably arise from thermal cleavage of the Fe-C bond, followed by oxygenation of (OEP)Fe and coupling of phenyl radicals.⁷³ Further, it has been shown that the reaction of (TTP)Fe(aryl) with O₂ in either CDCl₃ or CD₂Cl₂ solution results in the formation of O₂⁻, [(TTP)Fe(aryl)]⁺, and some (TTP)FeCl.⁷⁷

The present case involving (TTP)CrR is perhaps most similar to a previous study involving the preparation of (TPP)Ti(C₆H₅) and its interaction with molecular oxygen in toluene solution.⁹ Here, the products were (TPP)Ti(O) and biphenyl. Initial coordination of O₂ by the porphyrin complex was postulated, followed by a series of reaction steps similar to eqs 2-4.⁹ Clearly, the nature of the central metal ion is attenuating the reactivity of the M-C bond of the organometallic porphyrin complexes toward dioxygen.

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Reactivity of the Cr-C Bond toward Other Reagents. The reactivity of the Cr-C(aryl) σ-bond toward various reagents and conditions such as heat, light, acid, molecular iodine, and mercury(II) chloride was examined briefly. The aryl complexes could be heated in C₆D₆ at 130 °C in a sealed NMR tube and recovered unchanged. Anaerobic exposure of a CDCl₃ solution of (TTP)Cr(C₆H₅) to light gave (TTP)CrCl and C₆H₅D, through an apparently free radical process, since phenyl radicals are known to have an almost exclusive preference for abstracting hydrogen from CHCl₃.⁵⁵

The aryl complexes are relatively stable to water but are decomposed by acetic acid to give a new complex that has an electronic spectrum⁷⁸ which is similar to that reported for (TTP)Cr(O₂CCH₃).⁷⁹ These results suggest that the Cr-C₆H₅ bond has undergone acidolysis, a known reaction of Cr-C σ-bonds.³⁰

The arylchromium complexes also react with electrophiles such as mercury(II) chloride and molecular iodine in CDCl₃ in the expected manners.^{30,80} ¹H NMR experiments confirm that the reaction of (TTP)Cr(aryl) with HgCl₂ gives (TTP)CrCl and (aryl)HgCl, while reaction with I₂ gives the corresponding aryl iodide and presumably (TTP)CrI.⁸¹

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(81) The metalloporphyrin complex could possibly be (TTP)CrCl; the ¹H NMR resonances for (TTP)CrX (X = I or Cl) are essentially identical.²⁴