conversion of UO_3 to UO_2F_2 after 45 h at 180 °C. The presence of CsF does not give rise to further fluorination. The conditions and yields of our fluorinations are included in Table I.

With the exception of V_2O_5 that formed only VOF_3, group 5 oxides (M_2O_5) formed pentafluorides in essentially quantitative yield at $\sim$200 °C. In group 6, MoO_3 and WO_3 easily gave $MoOF_4$ and WOF_4 at $\sim$180–190 °C. Earlier, CrO_3 was shown to be converted quantitatively to CrO_2F_2.[4] Further fluorination of CrO_2F_2 with COF_2 either at higher pressure and higher temperature or by using anhydrous hydrogen fluoride as solvent was not possible. CrO_2F_2 was invariably recovered in quantitative yield. Commercial samples of WO_3 did not react with COF_2.

Oxides of groups 5, 6, and 16 show increasing reactivity with COF_2 on moving down the groups. However, in the case of group 14 dioxides, fluorination to MF_4 occurred with decreasing ease moving from SiO_2 to GeO_2, and finally, fluorination of SnO_2 occurred only at 220 °C in the presence of catalytic amounts of CsF. Lead(IV) oxide did not react. Carbonyl fluoride with P_4O_{10} gave a mixture of POF_3 and PF_5 (65% yield). In group 16, SO_2 did not react with COF_2 at 200 °C even in the presence of CsF and with longer reaction time (86 h). The reactions of COF_2 with either SeO_2 or TeO_2 proceed smoothly to form $SeOF_2$ or TeF_4 under conditions similar to those when SF_4 is used as a fluorinating reagent.

Fluorination of both I_2O_5 and B_2O_3 occurred very cleanly and at relatively low temperature. Trap-to-trap distillation gave pure IF_5 in 60% yield.

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Registry No. COF_2, 353-50-4; V_2O_5, 1314-62-1; Nb_2O_5, 1313-96-8; Ta_2O_5, 1314-61-0; PF_5, 7647-19-0; MoO_3, 1313-27-5; WO_3, 1314-35-8; MnO_2, 1313-13-9; OsO_4, 20816-12-0; Co_2O_3, 1308-04-9; NiO, 1313-99-1; HgO, 21908-53-2; B_2O_3, 1303-86-2; SiO_2, 7631-86-9; GeO_2, 1310-53-8; SnO_2, 18282-10-5; PbO_2, 1309-60-0; P_4O_{10}, 16752-60-6; SO_2, 7446-09-5; SeO_2, 7446-08-4; TeO_2, 7446-07-3; I_2O_5, 12029-98-0; UO_3, 1344-58-7; VOF_3, 13709-31-4; NbF_5, 7783-68-8; TaF_5, 7783-71-3; OPF_3, 13478-20-1; $MoOF_4$, 14459-59-7; WOF_4, 13520-79-1; BF_3, 7637-07-2; SiF_4, 7783-61-1; GeF_4, 7783-58-6; SnF_4, 7783-62-2; $SeOF_2$, 7783-43-9; TeF_4, 15192-26-4; IF_5, 7783-66-6; UO_2F_2, 13536-84-0.

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Synthesis of Tetramesitylporphyrin

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Metalloporphyrins have been largely used as oxygenation (i.e. hydroxylation and epoxidation) catalysts during the last 8 years.[1,2] They have been associated to various oxygen sources: PhIO, NaOCl, H_2O_2, ROOH, $KHSO_5$, or O_2 and electrons.

Efficient catalytic reactions are observed when the manganese or iron porphyrin is not transformed into an inactive μ-oxo entities or bleached via an intra- or intermolecular oxidation. This deactivation of the catalyst is very often avoided by using bulky porphyrin ligands in order to create a cage (in most cases it is an open well) around the active metal–oxo species. Such an open well effect has been obtained by using 2,6-disubstituted phenyl groups attached to the meso positions of synthetic porphyrins. Two ligands of this type have been largely used: tetramesitylporphyrin ($TMPH_2$) and tetrakis(2,6-dichlorophenyl)porphyrin in these metalloporphyrin-mediated oxygenation reactions.[3-8] The cage created by the methyl groups of the tetramesitylporphyrin allows also the isolation and characterization of high-valent metal–oxo species in the case of iron[9-11] or manganese[12,13] complexes.

The only limitation for general use of these bulky porphyrins is the tedious preparation according to the old Rothemund synthesis (aldehyde, pyrrole, and pyridine in a sealed tube) and its variations.[14,15] After purification, the yield of $TMPH_2$ preparation is in the range of 3–5%.[4] The recent report of Lindsey et al. of a new route for the preparation of tetraphenylporphyrins (preequilibration of pyrrole and benzaldehyde to the porphyrinogen at room temperature followed by an oxidation by a quinone under mild conditions) prompted us to try this new methodology in the preparation of a bulky porphyrin like $TMPH_2$.[16] Since we found that the yield of $TMPH_2$ by Lindsey's method reached 20%, but is sensitive to some experimental conditions, we wish to report in the present note the details of this preparation of $TMPH_2$ after modifications.

Experimental Section

Materials. Pyrrole (purum, Fluka) and mesitaldehyde (98%, Aldrich) were distilled under reduced pressure before use. 2,2-Dimethoxypropane, tetrachloro-*p*-benzoquinone (*p*-chloranil), and boron trifluoride–methanol complex were purchased from Janssen Chimica and used without further purification. Dichloromethane was distilled from CaH_2 under nitrogen before use. Alumina (activity I, neutral) was purchased from Merck.

Results

Synthesis of $TMPH_2$. A 1-L two-necked, round-bottom flask fitted with a reflux condenser and an argon inlet tube was filled with 500 mL of freshly distilled dichloromethane under a slight stream of argon and was magnetically stirred. Pyrrole (350 μL, 5 mmol), 2,2-dimethoxypropane (700 μL, 5.5 mmol), mesitaldehyde (750 μL, 5.5 mmol), and $BF_3{\cdot}CH_3OH$ (100–200 μL, 0.91–1.82 mmol) were added in this order by use of syringes. After addition of $BF_3{\cdot}CH_3OH$ the reaction mixture changes immediately from colorless to red-brown. The solution was stirred for 45 min at room temperature under a slow stream of argon. Then the solution was heated at 40 °C, tetrachloro-*p*-benzoquinone (400 mg, 1.6 mmol) was added, and the reaction mixture was maintained at slight reflux for 1 h (without argon bubling). After evaporation of the solution to dryness, the residue was redissolved in a minimum of CH_2Cl_2 and purified by chromatography over two successive dry columns of neutral alumina. From the first column (3.5 × 15 cm) with CH_2Cl_2 as eluent, one collected the first pink and green bands, combined these fractions, and evaporated them to dryness. The second chromatography column (3.5 × 15 cm) with toluene as solvent, gave first of all a pink band,

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Table I. Dependence of the Preparation Yield of $TMPH_2$ on the Quantities of *p*-Chloranil Used in the Oxidation Step[a]

mg of *p*-chloranil (mmol; equiv with respect to pyrrole)	$TMPH_2$ yield, %
200 (8.3; 0.17)	15
400 (1.67; 0.33)	20
600 (2.5; 0.5)	15
1200[b] (5; 1)	2-8

[a] The reagent quantities used are the ones indicated in the Experimental Section. [b] This amount of *p*-chloranil is the one used by Lindsey et al. in a preliminary communication: Lindsay, J. S.; et al. *Tetrahedron Lett.* **1986**, *27*, 4969.

which contains the pure mesitylporphyrin. The second pink-yellow band, already containing small amounts of *p*-chloranil, was also collected and combined with the crude reaction mixture of other preparations of $TMPH_2$. The first pink band was evaporated to dryness, recrystallized from distilled CH_2Cl_2 and dried under vacuum. One obtained 200 mg (yield: 20%) of the pure mesitylporphyrin. Purity of the sample has been checked by elemental analysis,[17] and the UV-visible spectrum was identical with that previously reported.[14] The IR spectrum did not show any traces of *p*-chloranil.

Discussion

Lindsey's preparation[16] was modified by using the methanol adduct of borontrifluoride and 2,2-dimethoxypropane to scavenge all possible traces of water during the reaction. We found that the reproducibility of the preparation described above is highly dependent on several factors.

(i) The first factor is the age of purchase and time of opening of the bottle of BF_3 catalyst. Three months after opening the $BF_3 \cdot CH_3OH$ bottle, 50% of its catalytic activity is already lost. The reported quantity of $BF_3 \cdot CH_3OH$ corresponds to that one of a freshly opened bottle.

(ii) The second factor is the amount of *p*-chloranil used in the second step (Table I). The best yield is obtained for 0.33 equiv of quinone oxidant with respect to pyrrole. When a large quantity of *p*-chloranil is employed, the formed porphyrin is partially destroyed by overoxidation, and furthermore the removal of all the quinone is difficult, even after two chromatography columns.

(iii) Third, the porphyrinogen equilibration is obtained within 45 min. The prolongation of that period usually leads to a reduced yield in $TMPH_2$.

(iv) Finally, overheating in the oxidation step must be avoided. A gentle reflux reduced the oxidative degradation of the formed porphyrin. The temperature control is even more crucial when a larger amount of *p*-chloranil is used.

However the yield of the reaction does not seemed to be influenced by shielding the reaction solution from ambient lighting.

In conclusion, the present synthesis of $TMPH_2$ leads to a respectable yield (20%) for such a sterically hindered porphyrin which is one of the favorite ligands used in metalloporphyrin-mediated catalytic oxygenations of hydrocarbons. The same procedure can be extended to the synthesis of tetrakis(2,6-dichlorophenyl)porphyrin.

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Note Added in Proof. During the submission procedure for the present note, a similar preparation has been reported by Lindsey et al. using the same modifications presented here.[18]

Registry No. $TMPH_2$, 56396-12-4; pyrrole, 109-97-7; mesitaldehyde, 487-68-3.

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(17) Anal. Calcd for $C_{56}H_{54}N_4$ (mol wt 782.62): C, 85.90; H, 6.95; N, 7.16. Found: C, 85.69; H, 7.24; N, 6.88.

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Anion Effects on the Hydrolysis of the (μ-Oxo)bis(pentaamminechromium(III)) Ion in Basic Solution

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Although the electronic structures of the (μ-oxo)bis(pentaamminechromium(III)) ion and related linear, oxo-bridged dimers have been probed extensively through spectroscopic and magnetic measurements,[1-3] the reaction chemistry of rhodo and erythro chromium dimer species is not well understood. In particular, the thermodynamic and mechanistic basis for the most characteristic reaction of the basic rhodo dimer, hydrolysis to the hydroxo erythro ion (eq 1) in alkaline media, is not fully revealed in the

$$[(NH_3)_5Cr]_2O^{4+} + H_2O \rightarrow (NH_3)_5Cr(OH)Cr(NH_3)_4(OH)^{4+} + NH_3 \quad (1)$$

several mechanistic studies of this process reported to date.[4-6] Having established the stoichiometry of reaction 1, Wilmarth and co-workers[4] suggested that negative charge buildup on chromium owing to pπ(O)–dπ(Cr) bonding is responsible for the weakening of a Cr–N bond and ultimately displacement of NH_3. Similarly, Schwarzenbach and Magyar attribute the first-order decay of the basic rhodo cation ($k = 1.6 \times 10^{-2}$ s^{-1}, 20 °C) to a trans effect of the bridging oxide ion.[6] A weak inhibitory effect of hydroxide ion was reported in an earlier study of the basic rhodo decay rate,[5] leaving the existence of a OH^--dependent term in the rate law uncertain.

Our group has explored the acid hydrolysis mechanism of the (μ-oxo)bis(pentaaquachromium(III)) cation (aqua dimer), a close relative to the basic rhodo ion, and documented unexpected sensitivity of the rate to the presence of reducing agents and anions.[7,8] We report here studies of anion and temperature effects on the rate of reaction 1. Of particular interest is the possibility that the Jahn–Teller effect may account for the intrinsic instability of the basic rhodo ion toward loss of ammonia, coupled with protonation of the bridging oxygen atom and bending of the Cr–O–Cr structural unit. A kinetic trans effect is ruled out by the finding[9] that *cis*-$[Cr(NH_3)_5(OH)Cr(NH_3)_4(OH)]^{4+}$ is the sole chromium-containing hydrolysis product of the basic rhodo cation.

Experimental Section

The acid rhodo bromide salt $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Br_5 \cdot 2H_2O$ was prepared through the aerobic oxidation of chromous bromide in concentrated aqueous ammonia, followed by acidification of the product mixture with HBr.[10] A 1 M chromous bromide stock solution was prepared by the addition of Aldrich Gold Label chromium chunks to anaerobic (N_2-purged) 2 M HBr. The crude acid rhodo product was recrystallized twice by dissolving in cold, 1 mM HBr and slowly adding cold, 1 M HBr. Anal. Calcd for $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Br_5 \cdot 2H_2O$: Cr, 14.3; N, 19.27; H, 4.85. Found: Cr, 14.9; N, 19.33; H, 4.96.

Reagent grade chemicals were used throughout, and solutions were prepared with triply distilled water. Kinetic measurements were made on a Durrum D-110 stopped flow apparatus, interfaced to an Apple II

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