Table IV. IR and NMR Data

| compd | IR[a] | NMR[b] P($CH_3$)$_3$ | NMR[b] Ph–Si | NMR[b] other |
|---|---|---|---|---|
| $(PMe_3)_3Rh(SiPh_3)$ (**1**) | | 0.88 (s) | 7.1 (m), 7.21 (t, 7), 8.12 (d, 7) | |
| $(PMe_3)_3H_2Rh(SiPh_3)$ | 1958 (br) | 0.78 (d, 6.0), 1.13 (d, 6.0) | 7.1 (m), 7.23 (t, 7), 8.01 (d, 7) | Rh–H, −10.1 (d, 117, of pseudo t, 16) |
| $(PMe_3)_3(CH_3)(H)(SiPh_3)Ir$ (**2–Ir**) | | 0.69 (d, 7.0), 1.08 (d, 7.5), 1.15 (d, 7.0) | 7.1 (m), 7.24 (t, 7), 8.10 (d, 7) | Ir–H −11.8 (d, 123, of t, 14.5),<br>Ir–$CH_3$ 0.14 (ddd, 12.7, 9.4, 3.6) |
| $(PMe_3)_2(CO)_2Rh(SiPh_3)$ | 1980 (s),<br>1930 (vs)[c] | 0.86 (t, 3.5) | 7.1 (m), 7.2 (m), 7.9 (m) | |
| $(PMe_3)_3I_2Rh(CH_3)$[d] | | 1.57 (d, 9.6), 1.85 (t, 3.4) | | Rh–$CH_3$ 1.00 (q, 5.0, of d, 2.0) |
| $CH_3SiPh_3$ | | | 7.1 (m), 7.5 (m) | 0.69 (s) |
| $CH_3CH_2SiPh_3$ | | | 7.1 (m), 7.5 (m) | 1.08 (pseudo t, 8), 1.24 (pseudo q, 8) |
| $CH_2{=}CHSiPh_3$ | | | 7.1 (m), 7.6 (m) | 5.77 (dd, 20.2, 3.7), 6.11 (dd, 14.5, 3.7), 6.60 (dd, 20.2, 14.5) |

[a] Nujol mull. Frequencies in $cm^{-1}$. [b] $C_6D_6$ solutions unless otherwise noted. Chemical shifts in ppm downfield from external $Me_4Si$; coupling constants in Hz given in parentheses. [c] Transparent; 1480–1900 $cm^{-1}$. [d] Tetrahydrofuran-$d_8$ solution.

Table V. Crystallographic Data for $Rh(SiPh_3)(PMe_3)_3$ (**1**)

| | |
|---|---|
| formula $C_{27}H_{42}P_3RhSi$ | space group $P2_1/n$ (no. 14) |
| fw 590.55 | $T = -70$ °C |
| $a = 9.433$ (3) Å | $\lambda = 0.71069$ Å (Mo K$\alpha$) |
| $b = 17.692$ (2) Å | $\rho_{calcd} = 1.337$ g cm$^{-3}$ |
| $c = 17.673$ (5) Å | $\mu = 7.87$ cm$^{-1}$ |
| $\beta = 96.03$ (1)° | transm coeff = 0.70–0.75 |
| $V = 2933.1$ Å$^3$ | $R(F_o) = 0.027$ |
| $Z = 4$ | $R_w(F_o) = 0.027$ |

Table VI. Fractional Coordinates (×10$^4$) and Equivalent Isotropic Thermal Parameters

| atom | $x$ | $y$ | $z$ | $B_{eqv}$, Å$^2$ |
|---|---|---|---|---|
| Rh(1) | 3542.3 (2) | 3534.7 (1) | 2412.6 (1) | 1.6 (1) |
| P(1) | 3422.8 (7) | 3909.5 (4) | 3630.6 (3) | 2.1 (1) |
| P(2) | 1807.4 (7) | 4364.1 (4) | 1864.6 (4) | 2.2 (1) |
| P(3) | 3265.6 (7) | 2595.2 (4) | 1533.8 (4) | 2.2 (1) |
| Si(1) | 5980.4 (7) | 3331.0 (3) | 2604.5 (3) | 1.7 (1) |
| C(1) | 4707 (3) | 3643 (2) | 4429 (2) | 3.5 (1) |
| C(2) | 1840 (3) | 3446 (2) | 3927 (2) | 3.4 (1) |
| C(3) | 3122 (6) | 4889 (2) | 3912 (2) | 4.7 (1) |
| C(4) | 2607 (4) | 5305 (2) | 1865 (2) | 3.3 (1) |
| C(5) | 1188 (4) | 4312 (2) | 847 (2) | 4.1 (1) |
| C(6) | 109 (4) | 4566 (2) | 2235 (2) | 4.2 (1) |
| C(7) | 4253 (3) | 1715 (2) | 1703 (2) | 3.2 (1) |
| C(8) | 1453 (3) | 2223 (2) | 1525 (2) | 3.9 (1) |
| C(9) | 3452 (5) | 2696 (2) | 524 (2) | 4.0 (1) |
| C(11) | 6926 (2) | 4159 (1) | 3150 (1) | 1.9 (1) |
| C(12) | 6557 (3) | 4901 (1) | 2951 (2) | 2.9 (1) |
| C(13) | 7172 (4) | 5520 (2) | 3344 (2) | 3.8 (1) |
| C(14) | 8161 (3) | 5408 (2) | 3963 (2) | 3.7 (1) |
| C(15) | 8538 (3) | 4684 (2) | 4180 (2) | 3.2 (1) |
| C(16) | 7947 (3) | 4070 (2) | 3776 (1) | 2.4 (1) |
| C(21) | 6659 (2) | 3397 (1) | 1621 (1) | 1.9 (1) |
| C(22) | 6282 (3) | 4023 (2) | 1161 (1) | 2.8 (1) |
| C(23) | 6674 (4) | 4095 (2) | 426 (2) | 3.6 (1) |
| C(24) | 7439 (3) | 3527 (2) | 124 (2) | 3.8 (1) |
| C(25) | 7823 (3) | 2901 (2) | 556 (2) | 3.4 (1) |
| C(26) | 7437 (3) | 2840 (2) | 1294 (2) | 2.6 (1) |
| C(31) | 6910 (3) | 2465 (1) | 3076 (1) | 2.2 (1) |
| C(32) | 6158 (4) | 1927 (2) | 3447 (2) | 3.1 (1) |
| C(33) | 6847 (5) | 1301 (2) | 3801 (2) | 4.3 (1) |
| C(34) | 8285 (5) | 1209 (2) | 3796 (2) | 4.9 (1) |
| C(35) | 9063 (4) | 1729 (2) | 3442 (2) | 4.3 (1) |
| C(36) | 8378 (3) | 2348 (2) | 3087 (2) | 2.9 (1) |

## Experimental Section

All reagents and compounds are air-sensitive, and manipulations were carried out at room temperature under an inert atmosphere (typically in a nitrogen-filled drybox) and with the use of dried, degassed solvents. $RhMe(PMe_3)_x$ ($x = 3, 4$)[7,13] and $IrMe(PMe_3)_4$[13] were prepared as previously described; other reagents were obtained commercially. C, H analyses were performed by Galbraith Laboratories. $^1H$ NMR spectra of all compounds were recorded at ambient probe temperature by using GE QE-300 spectrometers. These data are presented in Table IV together with selected IR data.

**(Triphenylsilyl)tris(trimethylphosphine)rhodium(I) (1).** A toluene solution (15 mL) containing 0.84 g of $RhMe(PMe_3)_x$ was treated with 0.52 g of $HSiPh_3$. The solution immediately turned red; after being stirred 1 h at room temperature, the solution was concentrated to 2 mL, pentane (15 mL) was added, and a red microcrystalline precipitate formed; this was isolated after 30 min; yield 0.79 g (67%). Anal. Calcd for $C_{27}H_{42}P_3RhSi$: C, 54.92; H, 7.17. Found: C, 54.94; H, 7.21. In a separate experiment, $RhMe(PMe_3)_x$ (0.042 g) and $HSiPh_3$ (0.026 g) were combined in 1 mL of deuteriobenzene, and the formation of compound **1** and methane was confirmed by NMR spectroscopy. Irregular blocks of crystalline compound **1** grew from the solution after 1 day at room temperature.

Reactions of compound **1** with carbon monoxide or dihydrogen were observed by bubbling the respective gas through deuteriobenzene solutions of compound **1**; in each case the red color bleached rapidly and the respective product was detected in >80% yield by $^1H$ NMR spectroscopy (see Scheme I and Table IV). Analytically pure compounds were obtained by recrystallization from benzene/hexane. Anal. Calcd for $H_2Rh(SiPh_3)(PMe_3)_3$: C, 54.73; H, 7.48. Found: C, 54.69; H, 7.47. Calcd for $Rh(CO)_2(SiPh_3)(PMe_3)_2$: C, 54.74; H, 5.83. Found: C, 54.75; H, 5.89. In the reaction of compound **1** with ethylene, an uncharacterized mixture of rhodium compounds was formed, and only vinyltriphenylsilane could be identified among the products. Stirring an ether suspension of compound **1** with 2 equiv of methyl iodide for several hours resulted in its conversion to $(PMe_3)_3I_2Rh(CH_3)$. Anal. Calcd for $C_{10}H_{30}I_2P_3Rh$: C, 20.02; H, 5.04. Found: C, 19.87, 20.26; H, 5.11, 5.03.

**X-ray Data Collection and Structure Solution.** A single crystal of compound **1**, obtained as above, was sealed in a capillary under $N_2$, mounted on a Enraf-Nonius CAD4 diffractometer, and cooled to −70 °C under a $N_2$ stream. Crystal and refinement data are provided in Table V. The structure was solved and refined without difficulty; all non-hydrogen atoms were refined anisotropically, and their positional and equivalent isotropic thermal parameters are listed in Table VI.

**Supplementary Material Available:** Tables of full anisotropic thermal parameters, positional and isotropic parameters for hydrogen atoms, all interatomic distances and intramolecular angles, and a summary of crystallographic data (5 pages); a listing of $F_o$ vs $F_c$ (13 pages). Ordering information is given on any current masthead page.

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(12) It is conceivable that compound **1** reacts with ethylene such that actual insertion of ethylene into the Rh–Si bond never occurs. One possibility is oxidative addition of the vinyl C–H bond followed by reductive elimination of triphenylvinylsilane. See ref 6 and: Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5732–5744 and references therein for examples of vinyl C–H oxidative addition.

(13) Thorn, D. L. *Organometallics* **1982**, *1*, 197–204; **1986**, *5*, 1897–1903. Price, R. T.; Andersen, R. A.; Muetterties, E. L. *J. Organomet. Chem.* **1989**, *376*, 407–417.

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# Epoxidation of Alkenes by Oxo(5,10,15,20-tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphinato)chromium(V) in Aqueous Solution

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Of continuing interest is alkene epoxidation by hypervalent metalloporphyrins.[1] We recently employed chromium(V)–oxo porphyrins in studies of the stoichiometric epoxidation of a number of alkenes as a means of judging the importance of alkene-derived $\pi$-cation-radical species as intermediates (in $CH_2Cl_2$).[1k] Much has been learned from investigations of the reaction of water-soluble metalloporphyrins in aqueous solution, since conditions of acidity, ionic strength, etc. are best maintained in this milieu.[2] The question has arisen as to the feasibility of studying alkene epoxidation by hypervalent metal–oxo porphyrin species in water. We report a study on the reaction of the water soluble oxo-(5,10,15,20-tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphinato)chromium(V) ((**1**)$\mathrm{Cr^{V}(O)(X)}$) with the water-soluble alkenes 3-cyclohexene-1-carboxylic acid and 2-cyclopentene-1-acetic acid in aqueous solution.

## Experimental Section

**Materials. 2-Cyclopentene-1-acetic acid** was purchased from Aldrich and purified by vacuum transfer. **3-Cyclohexene-1-carboxylic acid** was prepared as described in a previous study.[2f] Epoxide standards were prepared by esterification of the alkenes with ethereal diazomethane followed by treatment with *m*-chloroperbenzoic acid.

**5,10,15,20-Tetrakis(2,6-dimethylphenyl)porphine** was synthesized by the method of Lindsey and co-workers.[3] **5,10,15,20-Tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphine ((1)$H_2$)** was synthesized by using the procedure of Zipplies and Bruice.[2a] **(5,10,15,20-Tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphinato)chromium(III) hydrate** ((**1**)$\mathrm{Cr^{III}(H_2O)_2}$) was prepared by metalation of (**1**)$H_2$ (61 mg; 54 $\mu$mol) with chromium(II) chloride (2 × 1-g portions) in refluxing DMF (30 mL). After 1 h, aliquots checked by UV/vis spectroscopy showed no unreacted free base. The reaction mixture was cooled and evaporated to dryness, and the solid was dissolved in water. Concentrated aqueous NaOH was slowly added to the solution until no further $Cr(OH)_3$ precipitation was observed. Free chromium salts were removed by passing the solution through a Dowex-50W ion-exchange column ($H^+$ form), the eluate was neutralized and evaporated to dryness, and the solid was dissolved in methanol. To remove any porphyrin free base and residual salts, the methanolic solution was chromatographed on Sephadex 20L (preswollen) by using methanol as eluant. The eluate provided, after evaporation of the solvent, 9.3 mg of a dark green product [UV/vis [$\lambda_{max}$, nm (log $\epsilon$)]: (i) $H_2O$, pH 7, 392 (4.27), 450 (4.97), 574 (3.67), 618 (3.82), 637 (3.88); (ii) $H_2O$, pH 10, 387 (4.15), 441 (5.11), 569 (3.75), 611 (3.88), 630 (4.01)]. Anal. Calcd for $(C_{52}H_{40}N_4Na_4S_4O_{12})CrOH{\cdot}10H_2O{\cdot}6CH_3OH$ (fw = 1569.49): C, 44.39; H, 5.14; N, 3.57; S, 8.17; Cr, 3.31. Found: C, 44.65; H, 5.20; N, 3.25; S, 8.14; Cr, 2.79.

**Instrumentation.** All instrumentation employed in this investigation was described in a previous study.[1k]

**Electrochemistry.** Aqueous solutions of (**1**)$\mathrm{Cr^{V}(O)(X)}$ were generated by controlled-potential bulk electrolysis of (**1**)$\mathrm{Cr^{III}(H_2O)_2}$ ($6.4 \times 10^{-4}$ M, >0.1 M $NaClO_4$; approximate electrolysis time was 1 h and was monitored by UV/vis spectroscopy). Controlled-potential bulk electrolysis was carried out at 1.5 V (vs SCE) while argon was bubbled through the solution. The platinum-gauze electrode and Ag/AgCl reference electrode were cleaned by scanning (± limit 0.0–2.0 V) for 15 min in 10% $HNO_3$(aq) prior to each electrolytic preparation of (**1**)$\mathrm{Cr^{V}(O)(X)}$. Solutions of (**1**)$\mathrm{Cr^{IV}(O)}$ were obtained in the same manner (0.1 M $NaClO_4$) after electrolysis for a 10–20-min period.

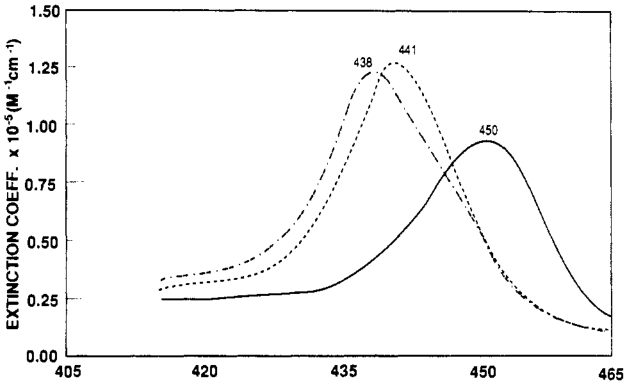

**Figure 1.** UV/vis spectra of (**1**)$\mathrm{Cr^{III}(H_2O)_2}$ ($\lambda_{max}$ = 450 nm at pH 6.25, —), (**1**)$\mathrm{Cr^{III}(H_2O)(HO)}$ ($\lambda_{max}$ = 441 nm at pH 11.2, ---), and (**1**)-$\mathrm{Cr^{III}(HO)_2}$ ($\lambda_{max}$ = 438 nm at pH 13.2, -·-·-), obtained during spectrophotometric titration experiments (argon, 30 °C).

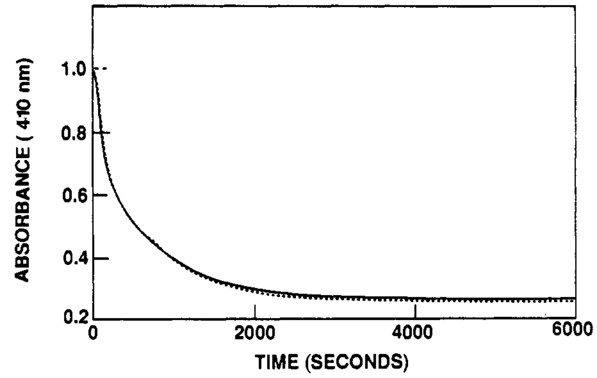

**Figure 2.** Computer-generated trace of the fit of experimental points for decrease in absorbance at 410 nm to the appropriate equation for two sequential first-order reactions ([(**1**)$\mathrm{Cr^{V}(O)(X)}$] = $1.5 \times 10^{-5}$ M, [2-cyclopentene-1-acetic acid] = $1.17 \times 10^{-2}$ M).

**Kinetic and Product Studies.** Kinetics of epoxidation were followed by using the electrochemically prepared chromium(V) porphyrin solutions with [(**1**)$\mathrm{Cr^{V}(O)(X)}$] at $1.5 \times 10^{-5}$ M (1.0-cm cuvettes) and $1.7 \times 10^{-4}$ M (0.1-mm cuvettes). Epoxide analyses were performed at the higher concentrations of oxidant by extraction of spent aqueous solutions with an ethereal diazomethane solution. The amount of recovered organic material was approximately 75%, and the yield of epoxide was adjusted to account for this loss in the extraction procedure. The ether phase was dried over $MgSO_4$ and evaporated to dryness, and the resultant residue was quantitatively transferred with $CH_2Cl_2$ to a 1.0-mL volumetric flask and subjected to GC analyses to determine the amount of epoxide methyl ester formed.

## Results

The water soluble and non $\mu$-oxo dimer forming 5,10,15,20-tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphinatochromium(III) species has been synthesized. The p$K_a$ values of (**1**)$\mathrm{Cr^{III}(H_2O)_2}$ were determined by spectrophotometric titration at 435, 441, and 450 nm (30 °C, argon) between pH 2.15 and 13.3. Plots of absorbance data points vs pH were constructed by computer fitting to the appropriate equation for the dissociation of a dibasic acid (eq 1) of p$K_{a1}$ = 9.0 ± 0.1 and p$K_{a2}$ = 12.6 ± 0.7. From the

$$(\mathbf{1})\mathrm{Cr^{III}(H_2O)_2} \overset{K_{a1}}{\rightleftharpoons} (\mathbf{1})\mathrm{Cr^{III}(H_2O)(HO)} + \mathrm{H^+} \quad (1a)$$

$$(\mathbf{1})\mathrm{Cr^{III}(H_2O)(HO)} \overset{K_{a2}}{\rightleftharpoons} (\mathbf{1})\mathrm{Cr^{III}(HO)_2} + \mathrm{H^+} \quad (1b)$$

spectrophotometric titration data the following spectral characteristics are assigned to the various chromium(III) porphyrin species (Figure 1): (**1**)$\mathrm{Cr^{III}(H_2O)_2}$ (pH 6.25), $\lambda_{max}$ = 450 nm, $\epsilon = 9.42 \times 10^4$ $M^{-1}$ $cm^{-1}$; (**1**)$\mathrm{Cr^{III}(H_2O)(HO)}$ (pH 11.2), $\lambda_{max}$ = 441 nm, $\epsilon = 1.27 \times 10^5$ $M^{-1}$ $cm^{-1}$; (**1**)$\mathrm{Cr^{III}(HO)_2}$ (pH 13.2), $\lambda_{max}$ = 438 nm, $\epsilon = 1.24 \times 10^5$ $M^{-1}$ $cm^{-1}$. After controlled-potential bulk electrolysis, the hypervalent chromium porphyrin species are characterized as follows (pH 4): (**1**)$\mathrm{Cr^{IV}(O)}$, $\lambda_{max}$ =

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(1) (a) $C_6H_5IO$/Fe: Groves, J. T.; Nemo, T. E.; Myers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032. (b) $C_6H_5IO$/Mn: Groves, J. T.; Kruper, W. J., Jr.; Haushalter, R. C. *Ibid.* **1980**, *102*, 6375. (c) $C_6H_5IO$/Cr: Groves, J. T.; Kruper, W. J.; Nemo, T. E.; Myers, R. S. *J. Mol. Catal.* **1980**, *7*, 169. (d) NaOCl/Mn: Guilmet, E.; Meunier, B. *Tetrahedron Lett.* **1980**, *21*, 4449. (e) *N*-oxide/Fe: Shannon, P.; Bruice, T. C. *J. Am. Chem. Soc.* **1981**, *103*, 4580. (f) *N*-oxide/Mn: Powell, M. F.; Pai, E. F.; Bruice, T. C. *Ibid.* **1984**, *106*, 3277. (g) Peracids/Fe: Groves, J. T.; Haushalter, R. C.; Nakamura, M.; Nemo, T. E.; Evans, B. J. *Ibid.* **1981**, *103*, 2884. (h) Peracids/Cr: Groves, J. T.; Kruper, W. J., Jr. *Ibid.* **1979**, *101*, 7613. (i) *t*-BuOOH/Mn: Balasubramanian, P. N.; Sinha, A.; Bruice, T. C. *Ibid.* **1987**, *109*, 1456. (j) Oxaziridine/Cr: Yuan, L.-C.; Bruice, T. C. *Ibid.* **1985**, *107*, 512. (k) Stoichiometric/Cr: Garrison, J. M.; Bruice, T. C. *Ibid.* **1989**, *111*, 191. Garrison, J. M.; Ostovic, D.; Bruice, T. C. *Ibid.* **1989**, *111*, 4960.

(2) (a) Zipplies, M. F.; Lee, W. A.; Bruice, T. C. *J. Am. Chem. Soc.* **1986**, *108*, 4433. (b) Bruice, T. C.; Zipplies, M. F.; Lee, W. A. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 4646. (c) Smith, J. R. L.; Balasubramanian, P. N.; Bruice, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 7411. (d) Bruice, T. C.; Balasubramanian, P. N.; Lee, R. W.; Smith, J. R. L. *Ibid.* **1988**, *110*, 7890. (e) Balasubramanian, P. N.; Smith, J. R. L.; Davies, M. J.; Kaaret, T. W.; Bruice, T. C. *Ibid.* **1989**, *111*, 1477. (f) Balasubramanian, P. N.; Lee, R. W.; Bruice, T. C. *Ibid.* **1989**, *111*, 8714.

(3) Lindsey, J. S.; Schreiman, I. C.; Hsu, H. S.; Kearney, P. C.; Marguerettaz, A. M. *J. Org. Chem.* **1987**, *52*, 827.

426 nm, $\epsilon = 5.18 \times 10^4$ M$^{-1}$ cm$^{-1}$; (**1**)Cr$^{V}$(O)(X), $\lambda_{max}$ = 410 nm, $\epsilon = 3.39 \times 10^4$ M$^{-1}$ cm$^{-1}$.

In the reaction of (**1**)Cr$^{V}$(O)(X) with 3-cyclohexene-1-carboxylic acid and 2-cyclopentene-1-acetic acid, a decrease in the $\lambda_{max}$ of the Cr$^{V}$–oxo species is observed, which is accompanied by an increase and then a decrease in the absorbance of the Cr$^{IV}$–oxo species and a continuing increase in absorbance of the Cr$^{III}$ species. These observations are in accord with previous studies of alkene epoxidation in an aprotic solvent ($CH_2Cl_2$) with various chromium(V)–oxo porphyrins (see discussion of kinetics in ref 1k). Reactions of (**1**)Cr$^{V}$(O)(X) with alkenes were monitored at the Soret band of this species ($\lambda_{max}$ = 410 nm). The decrease in $A_{410}$ is biphasic (Figure 2). The first phase (~70% decrease in $A_{410}$) is due to disappearance of (**1**)Cr$^{V}$(O)(X) and appearance of (**1**)Cr$^{IV}$(O) [i.e., (**1**)Cr$^{V}$(O)(X) epoxidizes alkene, in the rate-determining step, and is converted to (**1**)Cr$^{III}$($H_2O$)$_2$, which immediately reacts with remaining (**1**)Cr$^{V}$(O)(X) to provide 2 × (**1**)Cr$^{IV}$(O)]. The second phase corresponds to the disappearance of (**1**)Cr$^{IV}$(O) and appearance of (**1**)Cr$^{III}$($H_2O$)$_2$. The pseudo-first-order rate constants ($k_{obsd}$) for epoxidation were calculated from the change in $A_{410}$ with time during the first phase of reaction. The second-order rate constant, $k_2$ (=$k_{obsd}$/[alkene]), for reaction of (**1**)Cr$^{V}$(O)(X) ($1.5 \times 10^{-5}$ M) with 2-cyclopentene-1-acetic acid at $1.17 \times 10^{-2}$ M was calculated to be 0.16 M$^{-1}$ s$^{-1}$. The value of $k_2$ at [2-cyclopentene-1-acetic acid] = $4.61 \times 10^{-3}$ M and [(**1**)Cr$^{V}$(O)(X)] = $1.7 \times 10^{-4}$ M was determined to be 0.19 M$^{-1}$ s$^{-1}$. In the case of [3-cyclohexene-1-carboxylic acid] = $8.56 \times 10^{-3}$ M and [(**1**)Cr$^{V}$(O)(X)] = $1.7 \times 10^{-4}$ M, $k_2$ = 2.0 M$^{-1}$ s$^{-1}$.

The percentage yield of epoxide products were determined from the kinetic runs at [(**1**)Cr$^{V}$(O)(X)] = $1.7 \times 10^{-4}$ M. When corrected for recovery, the yields of epoxide products based upon [(**1**)Cr$^{V}$(O)(X)]$_i$ were 21% for methyl 3,4-epoxycyclopentane-1-acetate and 53% for methyl 3,4-epoxycyclohexane-1-carboxylate. We were unable to determine if an endothermic comproportionation of 2 × (**1**)Cr$^{IV}$(O) could provide (**1**)Cr$^{III}$($H_2O$)$_2$ + (**1**)-Cr$^{V}$(O)(X), with the latter being trapped by alkene. If such comproportionation were inoperative, the yields of epoxide would be 100% for methyl 3,4-epoxycyclohexane-1-carboxylate and 42% for methyl 3,4-epoxycyclopentane-1-acetate.

## Conclusions

The second-order rate constants and epoxide product yields for reaction of oxo(5,10,15,20-tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphinato)chromium(V) ((**1**)Cr$^{V}$(O)(X)) with 3-cyclohexene-1-carboxylic acid and 2-cyclopentene-1-acetic acid have been determined in aqueous solution (30 °C). Recently, water-soluble manganese porphyrins have been employed to catalyze the epoxidation of 2,5-dihydrofuran using hypochlorite as oxidant in aqueous solution.[4] In this catalytic system, the yields of epoxide were 60 and 70%. We now present the results of the stoichiometric epoxidation of alkenes by a hypervalent metal–oxo porphyrin in aqueous solution. In $CH_2Cl_2$ (30 °C), the second-order rate constant for reaction of cyclohexene with oxo(5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphinato)chromium(V) ((Me$_{12}$TPP)Cr$^{V}$(O)(X)) was determined as $5.19 \times 10^{-3}$ M$^{-1}$ s$^{-1}$. This value, when compared to that for the second-order reaction of (**1**)Cr$^{V}$(O)(X) with 3-cyclohexene-1-carboxylic acid (2.0 M$^{-1}$ s$^{-1}$), shows that these reactions are favored in water. In water, the rate constant for reaction of (**1**)Cr$^{V}$(O)(X) with 3-cyclohexene-1-carboxylic acid is about 12-fold greater than that in the reaction with 2-cyclopentene-1-acetic acid. In $CH_2Cl_2$, the second-order rate constant for reaction of oxo(5,10,15,20-tetrakis(2,6-dibromophenyl)porphinatochromium(V) with cyclohexene is ~22-fold greater than the rate constant for reaction with cyclopentene. Therefore, the change in solvent has little effect on the ratio of rate constants.

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# Crystal Structure of [Ru(OEP–*N*-$C_6H_5$)($C_6H_5$)]($BF_4$). An Organometallic Porphyrin Complex Containing an *N*-$C_6H_5$ Group with an Agostic Hydrogen

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The so-called "suicide adducts"[1] of cytochrome $P_{450}$ result from the Fe-to-N migration of an alkyl or aryl group within the high-valent oxo–alkene or oxo–arene intermediate.[2] Analogous N-substituted porphyrin complexes[3-5] can be prepared by chemical and electrochemical means from synthetic metalloporphyrins. While Fe complexes have the most obvious biological relevance, information about the structural, spectroscopic, and chemical properties of related N-substituted complexes is of interest. Relatively few[4,5] N-substituted porphyrin complexes have been characterized by X-ray crystallography. As a part of our study[6] of the redox and reaction chemistry of Ru(OEP)($C_6H_5$)$_n$ complexes (OEP is octaethylporphyrin), we have observed that oxidation of Ru(OEP)($C_6H_5$)$_2$ leads to Ru-to-N migration of a $C_6H_5$ group. We report herein the crystal structure of [Ru(OEP–*N*-$C_6H_5$)($C_6H_5$)]($BF_4$), which contains a Ru–$C_6H_5$ group and a *N*-$C_6H_5$ group with an agostic hydrogen.[7]

## Experimental Section

**Materials and Methods.** All manipulations were performed in a Vacuum Atmospheres inert-atmosphere drybox with an $O_2$ level below 2 ppm (Model A0-316-C oxygen analyzer). Solvents were dried by distillation over Na/benzophenone (toluene) or $P_2O_5$ ($CH_2Cl_2$). $AgBF_4$ (Aldrich) was used as received. Ru(OEP)($C_6H_5$)$_2$ was prepared according to the method of James and Dolphin.[8]

**Synthesis of [Ru(OEP–*N*-$C_6H_5$)($C_6H_5$)]($BF_4$).** In a typical preparation 8 mg (0.041 mmol) of $AgBF_4$ was added to a well-stirred solution of 20 mg (0.025 mmol) of Ru(OEP)($C_6H_5$)$_2$ in 10 mL of toluene. The resulting brown suspension was stirred for 1 h and then filtered to yield

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