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Redox Chemistry of $Ru(OEP)(CH_3)_2$. Isolation of the Bridging Methylene Complex $Ru(OEP\text{-}N\text{-}\mu\text{-}CH_2\text{-})(CH_3)^+$

Organometallic porphyrin complexes[1-3] play crucial roles in suicide inactivation of cytochrome P-450[4] and are similar to vitamin B_{12}[5a] and analogues.[5b] Analogous organometallic complexes with synthetic porphyrins have been the subject of many chemical studies.[1-3] As Collman pointed out[1a] several years ago, the steric bulk and stability of the porphyrin ring promise to add some flavor to the chemistry of organometallic porphyrin complexes. This chemistry is indeed interesting and varied:[1-3] C–C bond formation, M–C bond homolysis, C–C and C–N bond scission within the porphyrin ring, M-to-N migration of aryl/alkyl ligands, and α-C–C bond scission of alkenes and alkynes. Reactions like the latter are particularly interesting, since an organic group is transformed by the metal center. The reports of the oxidative addition[6] of alkanes to $Rh_2(OEP)_2$ and $Ir_2(OEP)_2$ yielding organometallic species provide rare examples of the participation of porphyrin complexes in C–H bond activation processes.

As an extension to the electrochemical, chemical, and spectroscopic studies[3] of the redox and reaction chemistry of $Ru(OEP)(aryl)_n$ (n = 1, 2) complexes, we have investigated the corresponding alkyl complexes. This preliminary report describes some interesting aspects of the redox-induced reaction chemistry of $Ru(OEP)(CH_3)_2$, including isolation of a porphyrin complex with a bridging methylene, $Ru(OEP\text{-}N\text{-}\mu\text{-}CH_2\text{-})(CH_3)^+$.

$Ru(OEP)(CH_3)_2$ was prepared from $Ru(OEP)Cl_2$ using the literature procedure.[7] The cyclic voltammetric[8] response of $Ru(OEP)(CH_3)_2$ in THF, shown in Figure 1, reveals an irreversible oxidation at +0.65 V and an irreversible reduction at −1.39 V. Identification of the products of these electrochemical reactions is accomplished using sodium naphthalenide (NaNap) as a reductant or $AgBF_4$ as an oxidant, followed by spectroscopic analysis of the isolated product. Addition of a stoichiometric amount of NaNap to $Ru(OEP)(CH_3)_2$ leads to formation of $Ru(OEP)(CH_3)(THF)^-$,[9] indicating loss of $CH_3^{\bullet}$ from the nascent $Ru(OEP)(CH_3)_2^-$. Fast-scan cyclic voltammetry[8] indicates a lifetime for $Ru(OEP)(CH_3)_2^-$ of ~500 μs. Loss of a ligand from a reduced organometallic porphyrin complex is common, as with $C_6H_5^-$ from $Ru(OEP)(C_6H_5)_2^{2-}$,[3a,b] CH_3^- from $Co(OEP)(CH_3)^-$,[10a] $CH_3^{\bullet}$ from $Co(L)(CH_3)^-$ (L = macrocycle),[10b] and $C_8H_{13}^-$ from $Ir(OEP)(C_8H_{13})^{2-}$.[10c] The diamagnetic $Ru(OEP)(CH_3)(THF)^-$ complex can be prepared alternatively from $Ru(OEP)(CH_3)(THF)$ using NaNap. Oxidation of $Ru(OEP)(CH_3)(THF)$ with Ag^+ leads to a stable, paramagnetic cation, $Ru(OEP)(CH_3)(THF)^+$.[11] Scheme I illustrates these reactions of Ru(OEP)-

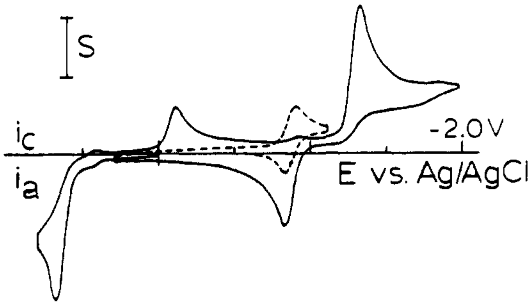

Figure 1. Cyclic voltammetric response of $Ru(OEP)(CH_3)_2$ in 0.2 M Bu_4NClO_4/THF at a Pt disk electrode (0.08 cm^2). S = 12.5 μA/cm^2. The scan was initiated in a positive direction from 0 V at 200 mV/s. A dashed line illustrates the second scan reversed at 0.3 V; the couple at −0.8 V is $[Ru(OEP)(CH_3)(THF)]^{0/-}$.

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[2] Reference 1 provides reviews with numerous references; recent, specific articles include the following: (a) Artaud, I.; Gregoire, N.; Leduc, P.; Mansuy, D. *J. Am. Chem. Soc.* **1990**, *112*, 6899. (b) Balch, A. L.; Chan, Y.-W.; Olmstead, M. M.; Renner, M. W.; Wood, F. E. *J. Am. Chem. Soc.* **1988**, *110*, 3897. (c) Ke, M.; Rettig, S. J.; James, B. R.; Dolphin, D. *J. Chem. Soc., Chem. Commun.* **1987**, 1110.

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[6] (a) Del Rossi, K. J.; Wayland, B. B. *J. Am. Chem. Soc.* **1985**, *107*, 7941. (b) Paonessa, R. S.; Thomas, N. C.; Halpern, J. *J. Am. Chem. Soc.* **1985**, *107*, 4333. (c) Del Rossi, K. J.; Wayland, B. B. *J. Chem. Soc., Chem. Commun.* **1986**, 1653.

[7] Sishta, C.; Ke, M.; James, B. R.; Dolphin, D. *J. Chem. Soc., Chem. Commun.* **1986**, 787.

[8] Cyclic voltammetry was performed under Ar or N_2 with a three-electrode configuration using either a Pt disk electrode (A = 0.08 cm^2) and a BAS CV-1 potentiostat for scan rates of 20–500 mV/s or a Pt disk microelectrode (d = 10 μm), a locally-constructed potentiostat, and a Tektronix 2430A storage oscilloscope for scan rates of 1–20 000 V/s. Solutions were ca. 2 mM in metalloporphyrin complex in 0.2 M Bu_4NClO_4/THF or 0.2 M Bu_4NClO_4/CH_2Cl_2. Lifetimes were estimated from relative peak currents (cf. Bard, A. J.; Faulkner, L. J. *Electrochemical Methods*; Wiley: New York, 1980; Chapter 4.

[9] $(Na)[Ru(OEP)(CH_3)]$: ^1H NMR (200 MHz, C_6D_6) δ −8.25 (br s, 3 H, Ru–CH_3), 1.75 (t, 24 H, OEP CH_3), 3.60 (q, 16 H, OEP CH_2), 8.55 (s, 4 H, H_{meso}).

[10] (a) Perree-Fauvet, M.; Gaudemer, A.; Boucly, P.; Devynck, J. *J. Organomet. Chem.* **1976**, *120*, 439. (b) Martin, B. D.; Finke, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 2419. (c) Cornillon, J.-L.; Anderson, J. E.; Swistak, C.; Kadish, K. M. *J. Am. Chem. Soc.* **1986**, *108*, 7633.

[11] $[Ru(OEP)(CH_3)(THF)](BF_4)$: ^1H NMR (300 MHz, CD_2Cl_2) δ −5.0 (br s, 4 H, THF), 7.6 (br s, 24 H, OEP CH_3), 15.8 (br s, 4 H, THF), 33.5 (br s, 4 H, H_{meso}), 63.0 (br s, 8 H, OEP CH_2), 84.5 (br s, 8 H, OEP CH_2).

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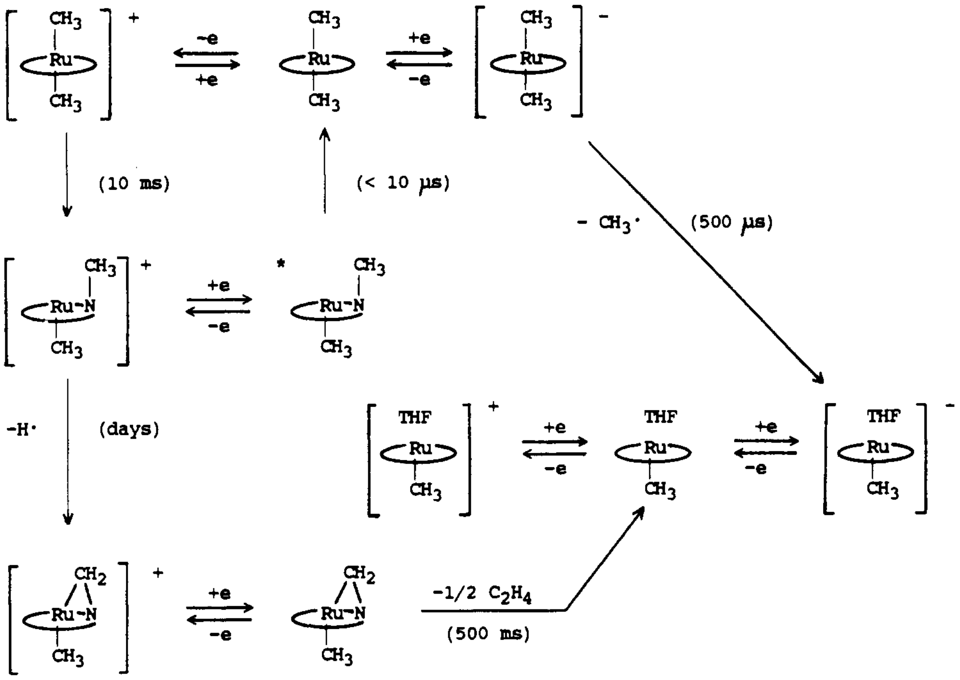
Scheme I. Redox Pathways of Ru(OEP)$(CH_3)_2$ and Ru(OEP)(CH_3)



* species not observed due to short lifetime.

(CH_3)(THF) and Ru(OEP)$(CH_3)_2$.

The irreversible anodic wave for the oxidation of Ru(OEP)$(CH_3)_2$ at +0.65 V is coupled to the irreversible cathodic wave at −0.16 V in Figure 1. Such behavior is common with iron, ruthenium, and cobalt porphyrin complexes[1b,4b] and is associated with two opposing EC pathways in a square scheme as illustrated in Scheme I. The lifetimes of the electrochemically-generated Ru(OEP)$(CH_3)_2^+$ and Ru(OEP-*N*-CH_3)(CH_3) species are ~10 ms and <10 μs, respectively, based on fast-scan cyclic voltammetry.[8] $AgBF_4$ oxidation of Ru(OEP)$(CH_3)_2$ provides verification of this square scheme and also reveals unexpected chemistry of oxidized alkyl porphyrin complexes. Oxidation of Ru(OEP)$(CH_3)_2$ with precisely 1 equiv of $AgBF_4$ leads to the expected paramagnetic Ru(OEP-*N*-CH_3)$(CH_3)^+$ species,[12] which is fairly stable (half-life of 60 d) under rigorously anhydrous and anaerobic conditions (evacuated and sealed NMR tube). Under more routine conditions (or in the presence of radical scavengers, vide infra) Ru(OEP-*N*-CH_3)$(CH_3)^+$ decomposes to a diamagnetic complex. The ^1H and ^2H NMR spectra[13] of this diamagnetic product (or the Ru(OEP)$(CD_3)_2$-derived analogue) indicate a "Ru(OEP)$(CH_3)(CH_2)$" complex. Crystallization of the product from CH_2Cl_2/benzene yields a low-quality crystal whose structure[14] can not be refined to better than $R_w = 0.2$. Despite its low quality, the crystal structure corroborates and clarifies the NMR results. The Ru(OEP-*N*-CH_3)$(CH_3)^+$ complex decomposes to a bridging CH_2 complex, Ru(OEP-*N*-μ-CH_2–)$(CH_3)^+$.

Cyclic voltammetry of [Ru(OEP-*N*-μ-CH_2–)(CH_3)][(BF_4) in CH_2Cl_2 reveals an irreversible reduction at −0.69 V. Cyclic voltammetry[8] reveals a lifetime of ca. 0.5 s for the electrochemically-generated Ru(OEP-*N*-μ-CH_2–)(CH_3) species. Chemical reduction with 1 equiv of NaNap produces Ru(OEP)(CH_3)(THF). Reduction of porphyrin complexes with C-based ligands bridging the metal and the porphyrin N typically results in formation of a carbene[1,2a] (often the original source of the oxidized, bridging complex). Such a process with Ru(OEP-*N*-μ-CH_2–)$(CH_3)^+$ would lead to a Ru=CH_2 species. Although M=CH_2 species have been prepared,[15] none are known for porphyrin complexes. James and Dolphin have postulated[2c] a Ru(OEP)$(CH_2)(CH_3)$ complex that rapidly decomposes to Ru(OEP)(CH_3) + $^1/_2C_2H_4$. Gas chromatographic analysis[16] of the headspace above the NaNap + Ru(OEP-*N*-μ-CH_2–)$(CH_3)^+$ reaction mixture reveals C_2H_4 and CH_4. Decomposition of a Ru(OEP)$(CH_2)(CH_3)$ intermediate is a plausible[15c] source of Ru(OEP)(CH_3)(THF) and C_2H_4.

The mechanism for transforming Ru(OEP)$(CH_3)_2$ to Ru(OEP-*N*-μ-CH_2–)$(CH_3)^+$ could be a two-step e^-/H•-transfer sequence as invoked by Hayes and Cooper[17] for the initial steps of the conversion of $Cp_2W(CH_3)_2$ to $Cp_2W(CH_2{=}CH_2)(H)$ or sequential 1-e^- oxidations and then deprotonation (similar to that uncovered for [Ni(TPP-*N*-$CH_2CO_2C_2H_5$)](ClO_4) by Callot et al.[18]). We favor the former on the basis of three observations. (1) substoichiometric oxidations with $AgBF_4$ yield Ru(OEP-*N*-μ-CH_2–)$(CH_3)^+$ rather than Ru(OEP-*N*-CH_3)$(CH_3)^+$, due to the presence of CH_3• from Ru–C bond homolysis of the unreacted

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(12) [Ru(OEP-*N*-CH_3)(CH_3)](BF_4): ^1H NMR (200 MHz, 4:1 CD_2Cl_2–C_6D_6) δ −3.9 (br s, 2 H, H_{meso}), −1.8 (s, 6 H, OEP CH_3), −1.1 (s, 6 H, OEP CH_3), −0.45 (br s, 2 H, OEP CH_2), 0.4 (s, 6 H, OEP CH_3), 1.75 (br s, 6 H, OEP CH_2), 3.2 (s, 6 H, OEP CH_3), 4.05 (br s, 2 H, OEP CH_2), 6.1 (br s, 2 H, H_{meso}), 6.35 (br s, 2 H, OEP CH_2), 9.3 (br s, 2 H, OEP CH_2), 11.4 (br s, 2 H, OEP CH_2), 19.2 (br s, 2 H, OEP CH_2), 21.6 (br s, 2 H, OEP CH_2), 71.1 (br s, 3 H, N–CH_3).

(13) [Ru(OEP-*N*-μ-CH_2–)(CH_3)](BF_4): ^1H NMR (200 MHz, CD_2Cl_2) δ −3.19 (s, 3 H, Ru–CH_3), −1.27 (s, 2 H, Ru–CH_2–N), 1.67 (t, 6 H, OEP CH_3), 1.77 (t, 6 H, OEP CH_3), 1.78 (t, 6 H, OEP CH_3), 1.85 (t, 6 H, OEP CH_3), 3.71 (q, 4 H, OEP CH_2), 3.72 (q, 4 H, OEP CH_2), 3.91 (q, 4 H, OEP CH_2), 4.01 (q, 4 H, OEP CH_2), 9.75 (s, 2 H, H_{meso}), 9.81 (s, 2 H, H_{meso}). Anal. Calcd for $C_{38}H_{49}N_4BF_4Ru$: C, 60.87; H, 6.59; N, 7.47; F, 10.14. Found: C, 61.39; H, 6.52; N, 6.68; F, 9.78.

(14) A brown-red crystal with approximate crystal dimensions of 0.5 × 0.2 × 0.1 mm was investigated on an Enraf-Nonius CAD4 diffractometer using previously described procedures.[3c] Attempts at solving the structure were undermined by slight disorder of the BF_4^- and CH_2Cl_2 within the crystal. See supplementary material for further information.

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(16) (a) Gas chromatographic analyses of the headspace were performed on a Porpak Q column. (b) 50% of the expected carbonaceous material was observed in the headspace as C_2H_4 and CH_4 with a molar ratio of 0.67:1. Given the solubilities of C_2H_4 and CH_4 in C_6H_6 and expected sampling and quantitation errors, we view these GC results as "nearly quantitative". For solubilities, see: *Solubilities of Inorganic and Organic Compounds*; MacMillin: New York, 1963.

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$Ru(OEP)(CH_3)_2$ (CH_4 is observed[16a] in the headspace). (2) Use of $(C_6H_5)_3C^+$ as an oxidant forms $(C_6H_5)_3CH$, resulting from H• abstraction from $Ru(OEP\text{-}N\text{-}CH_3)(CH_3)^+$. Verification of $Ru(OEP\text{-}N\text{-}CH_3)(CH_3)^+$ as the source of H• is provided by analogous experiments with $Ru(OEP)(CD_3)_2$; ^1H and ^2H NMR spectra indicate $(C_6H_5)_3CD$. (3) Addition of TEMPO,[19] a radical trap,[19a] but ineffective oxidant in aprotic media,[19b] to $Ru(OEP\text{-}N\text{-}CH_3)(CH_3)^+$ cleanly yields $Ru(OEP\text{-}N\text{-}\mu\text{-}CH_2\text{-})(CH_3)^+$. We are presently investigating the reactivity of these new alkyl porphyrin complexes.

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Supplementary Material Available: Figures showing ^1H NMR spectra of $Ru(OEP)(CH_3)(THF)^-$, $Ru(OEP)(CH_3)(THF)^+$, $Ru(OEP\text{-}N\text{-}CH_3)(CH_3)^+$, $Ru(OEP\text{-}N\text{-}\mu\text{-}CH_2\text{-})(CH_3)^+$, and the reaction mixture from the reaction of $Ru(OEP)(CH_3)_2$ with 0.25 equiv of $AgBF_4$, an ORTEP drawing, and a table of crystallographic parameters for $Ru(OEP\text{-}N\text{-}\mu\text{-}CH_2\text{-})(CH_3)^+$ (9 pages). Ordering information is given on any current masthead page.

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Detection of Coordinated Methyl and Ethyl Deuteron NMR Signals and Observation of Alkyl Group Interchange for Alkyliron(III) Porphyrin Complexes

Synthetic and reactivity studies of alkyl- and aryl-metalloporphyrins has become an active endeavor.[1] The alkyliron(III) porphyrin complexes can be prepared by three general routes:[1,2] (i) reaction of the corresponding Grignard or lithium reagent with the iron(III) halide complex; (ii) combination of the alkyl radical with the iron(II) complex; (iii) direct alkylation of the iron(I) porphyrin anion by alkyl halides. Alkyliron(III) porphyrins are relatively unstable, and over a period of several hours the iron(II) porphyrin appears, presumably as a product of Fe–C bond homolysis. Reactivity studies of paramagnetic alkyliron(III) porphyrins reveal unconventional organometallic pathways. For example, the apparent Fe–C insertion chemistry of alkyliron(III) porphyrins with CO is likely dictated by free radical reactions[3] reminiscent of those elucidated for CO insertion into the Rh–H bond of hyrdidorhodium porphyrins.[4] Mechanistic aspects of the much more facile O_2 insertion reaction of alkyliron(III) porphyrins are less clear with regard to disruption of the Fe–C bond.[5]

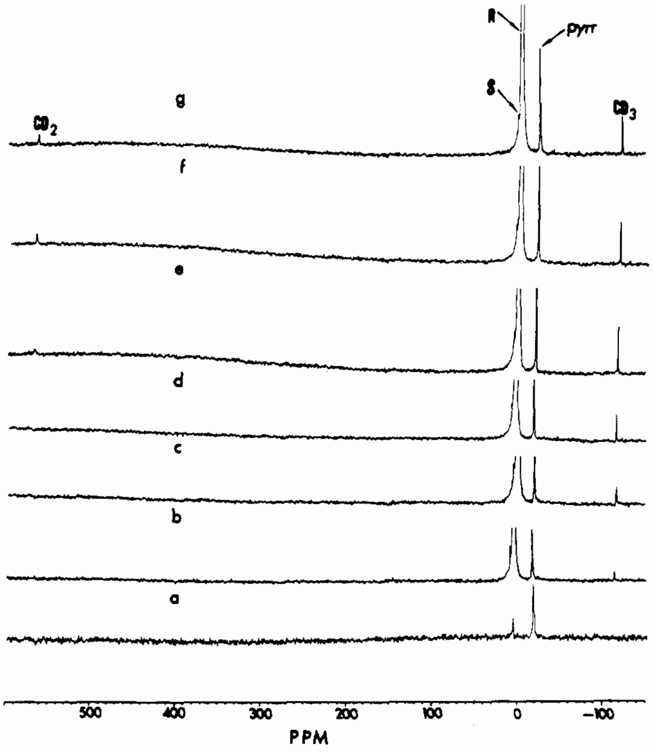

Figure 1. Deuterium NMR spectra (55 MHz) for time course of alkyl group interchange (toluene solvent, 25 °C, $Si(CD_3)_4$ reference): (a) 8 mM solution of (d_8-TPP)Fe(CH_3); (b–g) CD_3CD_2I concentration 0.52 M. Spectra were recorded at the following times after addition of CD_3CD_2I: (b) 20 min; (c) 30 min; (d) 90 min; (e) 120 min; (f) 180 min; (g) 240 min. Labels: R = excess CD_3CD_2I, S = solvent, pyrr = porphyrin pyrrole signal, and CD_2 and CD_3 are the alkyl ligand signals for (d_8-TPP)Fe(CD_2CD_3).

Nuclear magnetic resonance spectroscopy of the paramagnetic alkyliron porphyrins provides a useful analytical method for definition of the spin and ligation states. The low-spin iron(III) porphyrin pyrrole and alkyl ligand β- and γ-methylene proton NMR signals have been assigned,[2a] but the α-methylene (or methyl) signal has not been previously detected. Hence, this report describes use of deuterium NMR spectroscopy for detection of coordinated alkyl signals and for subsequent monitoring of an unusual alkyl–alkyl halide interchange reaction of alkyliron(III) porphyrins.

Methyl- and ethyliron(III) tetraphenylporphyrin (d_8-pyrrole) complexes were generated in situ under anaerobic conditions in 5-mm NMR tubes by addition of a stoichiometric quantity of the Grignard reagent (RMgCl in THF) to chloroiron(III) tetraphenylporphyrin in toluene solution. The alkyl derivatives and the deuteriated alkyl analogues were also prepared by oxidative addition of the iodoalkane to the iron(I) porphyrin anion generated in THF solution by $LiBH_4$ reduction.

Deuterium NMR spectra with a very wide spectral width revealed a previously undetected far downfield signal at 532 ppm (25 °C, toluene solvent) for the d_3-methyliron(III) tetraphenylporphyrin complex.[6] The analogous d_5-ethyl complex gave signals for the ethyl ligand at 562 and −117 ppm (toluene solvent).[6]

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(6) For THF solution at 25 °C the signals and line widths were as follows: for coordinated methyl, 509 ppm, 80-Hz line width; for ethyl, 548 and −100 ppm, 115- and 62-Hz line widths, respectively. Line widths were identical for toluene and THF solvents.

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