$Ru(OEP)(CH_3)_2$ (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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Department of Chemistry
Purdue University
West Lafayette, Indiana 47907-1393

Jeffery W. Seyler
Lance K. Safford
Phillip E. Fanwick
Charles R. Leidner*

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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]

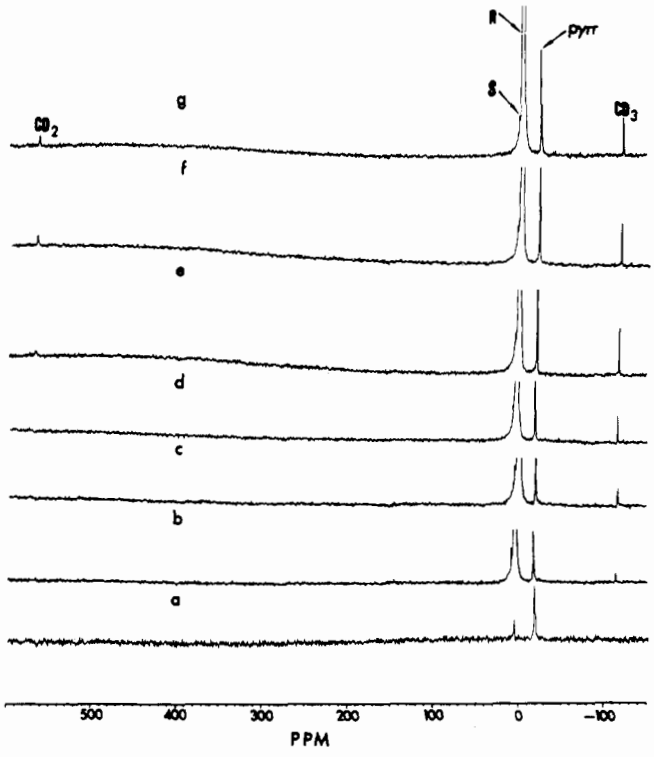

Figure 1. Deuterium NMR spectra (55 MHz) for time course of alkyl group interchange (toluene solvent, 25 °C, $Si(CD_3)_4$ reference): (a) 8 mM solution of $(d_8\text{-TPP})Fe(CH_3)$; (b–g) CD_3CD_2I concentration 0.52 M. Spectra were recorded at the following times after addition of CD_3CD_2I: (b) 20 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 $(d_8\text{-TPP})Fe(CD_2CD_3)$.

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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Intensities of the ethyl signals when compared to the deuteriated pyrrole signal at −17.6 ppm were consistent with the respective methylene and methyl assignments. A methyl proton NMR signal for the ethyliron(III) tetratolylporphyrin complex at −117 ppm (20 °C) has been reported recently.[5c] The far upfield and downfield deuterium signals exhibit Curie-like chemical shift behavior[7] with deviation from linearity at low temperature.

The ability to detect coordinated alkyl deuteron signals provided a convenient tool for demonstration of a novel alkyl interchange reaction. An 8 mM solution of (d_8-TPP)Fe(CH_3) was prepared in toluene by the Grignard route. An upfield pyrrole deuteron signal is seen for this species in Figure 1a. Within 5 min of preparation, excess C_2D_5I was added (to a concentration of 0.52 M) under anaerobic conditions. Deuterium spectra were recorded over a period of 4 h at 25 °C (each spectrum required only minutes for acquisition). Figure 1 reveals the appearance and growth of far downfield and upfield signals due to a coordinated d_5-ethyl group. The apparent half-life for this process for the specific solution conditions is approximately 100 min. In a separate proton NMR experiment (with d_8-toluene solvent) the expected appearance of CH_3I was confirmed.

The interchange process is independent of contamination by unreacted (TPP)FeCl (the precursor to the methyl complex), contamination by iron(II) porphyrin (generated by addition of excess Grignard reagent), or preparative route for the alkyliron(III) complex (Grignard route vs oxidative addition of RI to $TPPFe(I)^-$). In separate experiments the interchange of a proteo-alkyl ligand with a like deuterio-alkyl ligand was also demonstrated. Light is not required to effect the alkyl group interchange. No *N*-alkyliron porphyrin products are detected, and in the absence of oxidants and reductants there appears to be no relationship to the intramolecular alkyl exchange described for cobalt porphyrins.[8]

In separate experiments it was demonstrated that iron(II) tetraphenylporphyrin reacts slowly with alkyl iodides to produce equivalent amounts of the alkyliron(III) and iodoiron(III) derivatives. The high-spin (TPP)FeI complex exhibits a pyrrole deuteron NMR signal at 80 ppm. Absence of this signal for a period of days in solutions of (TPP)FeR and excess R'I indicates that the iron(II)/R'I reaction is not a significant route for alkyl group interchange.

One possible way to rationalize the interchange reaction between alkyliron(III) and iodoalkanes involves a known facile homolysis,[9] with subsequent alkyl radical iodine atom abstraction and radical–iron(II) recombination:

$$(TPP)Fe^{III}R \rightleftarrows (TPP)Fe^{II} + R^{\bullet} \quad (1)$$

$$R'I + R^{\bullet} \rightleftarrows RI + R'^{\bullet} \quad (2)$$

$$(TPP)Fe^{II} + R'^{\bullet} \rightleftarrows (TPP)Fe^{III}R' \quad (3)$$

However, as is described below, some conditions must be placed on this three-step mechanism in order to account for iodoalkane stabilization of the alkyliron(III) complex. The rate constant for the second reaction where R• is the methyl radical and R'I is iodoethane is 5.4×10^4 M^{-1} s^{-1} in toluene solvent at ambient temperature.[10] Hence, iodine atom abstraction is made competitive with rapid radical–iron(II) recombination (nearly diffusion controlled[11]) by virtue of the large excess of iodoalkane.

An unexpected feature of alkyliron(III) porphyrin chemistry in the presence of excess respective iodoalkane is the stabilization of the alkyliron(III) state. For example, the ethyliron(III) tetraphenylporphyrin complex is converted to the square planar iron(II) derivative with a half-life of less than 1 day,[12] but in the presence of 0.5 M iodoethane the half-life is extended to several days. The stabilization effect where R = R' (the "identity" reaction) may be explained in terms of the mechanism shown above provided one or more of the following conditions are met: (i) restriction of the reactions to a radical cage; (ii) preassociation of an iodoalkane with the iron porphyrin; (iii) formation of an R•/RI complex such that the radical would be sequestered from loss by coupling, disproportionation, or solvent hydrogen atom abstraction. The possibility of a radical cage or other concerted process may be suggested by literature reports that demonstrate the weak (and structurally undefined) complex formation between iodoalkanes and both iron(II)[13] and iron(III)[14] porphyrins.

The unusual stabilization effect has implications for crystal growth experiments with organometallic species that are prone to undergo metal–carbon homolysis. Alkyl group interchange provides yet another synthetic route for systems in which Grignard reactions or two-electron oxidative-addition reactions are problematic.

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Department of Chemistry
University of Iowa
Iowa City, Iowa 52242

Zijun Li
Harold M. Goff*

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Vibrational and Electrochemical Properties of a Series of Stable Manganese(V)–Oxo Complexes

The importance of manganese complexes of oxidation state IV and above can be seen in their roles in stoichiometric and catalytic oxidations and biological redox enzymes. The significance of the permanganate ion in stoichiometric oxidations in which manganese(V)–oxo complexes are intermediates is well documented.[1] Manganese(V)–monooxo complexes are believed to be active intermediates in oxo transfer and related reactions with porphyrin and salen catalysts.[2] In biological systems, manganese–oxo complexes have a possible role in the oxygen-evolving complex in photosynthesis.[3] Because of inherent high reactivity, evidence for the existence of terminal monooxo complexes of manganese has been difficult to obtain. Careful spectroscopic studies have elucidated the existence of $Mn^{IV}(O)$(porphyrin) compounds.[2a,4]

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