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Supplementary Material Available: A description of spectroscopic and analytical data for $[(\eta^2\text{-}CH_2{=}C{=}CPh)Ru(CO)_2Cp]BF_4$, $\overline{CH_2C(CN)_2C(CN)_2C(Ph){=}C}Ru(CO)_2Cp$, and complexes **1**-**6** and details of the structure determinations for complexes **2**, **4**, and **5**, including tables of crystal data and data collection parameters, general temperature factor expressions, positional parameters and their estimated standard deviations, and selected bond distances and angles (24 pages). Ordering information is given on any current masthead page.

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^{1}H Nuclear Magnetic Resonance Studies of the Reduction of Paramagnetic Iron(III) Alkyl Porphyrin Complexes to Diamagnetic Iron(II) Alkyl Complexes

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Summary: Reaction of (TPP)Fe^{III}Cl in dichloromethane with LiHBEt$_3$ yields (TPP)Fe^{III}Et.[15] Reduction of (TPP)-Fe^{III}R to [(TPP)Fe^{II}R]$^-$ (R = *n*-propyl, ethyl) by either LiHBEt$_3$ or KHB(*i*-Bu)$_3$ can be accomplished in benzene/tetrahydrofuran solution, where electron exchange between the iron(III) and iron(II) alkyls is rapid. [(TPP)Fe^{II}R]$^-$ is diamagnetic and is reoxidized by dioxygen to (TPP)Fe^{III}R.

The paramagnetic alkyl complexes of iron(III) porphyrins have received considerable study.[1-7] We have recently reported that in toluene solution at -80 °C dioxygen readily inserts into the Fe-C bond of low-spin ($S = {}^1/_2$) (P)Fe^{III}CR$_3$ to yield the very thermally unstable, high-spin ($S = {}^5/_2$) alkyl peroxide complex (P)Fe^{III}OOCR$_3$.[8,9] Electrochemical studies have shown that (P)Fe^{III}CR$_3$ can be reduced to the iron(II) level,[2,7] but other spectroscopic and reactivity data on the iron(II) alkyl complexes (P)-Fe^{II}CR$_3^-$ are lacking. Here we report on the chemical reduction of (P)Fe^{III}CR$_3$ and on the reactivity of these iron(II) alkyls toward dioxygen. Trialkylborohydride ions are effective reducing agents for this, and the general question of their reactivity toward iron prophyrins has been examined.

Treatment of (TPP)Fe^{III}Cl in dichloromethane solution with lithium triethylborohydride (Super-Hydride) in tetrahydrofuran solution at room temperature in the dark results in nearly quantitative conversion to (TPP)Fe^{III}C-H$_2$CH$_3$, which has been identified by its characteristic ^{1}H NMR resonances (pyrrole H, -18.9; methyl H, -117.2 ppm; at 23 °C in benzene). This represents an unusual case in

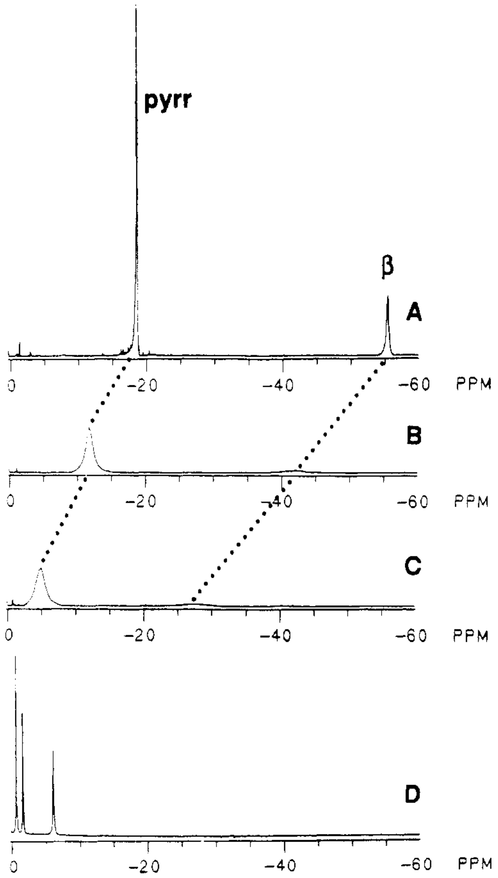

Figure 1. ^{1}H NMR spectra (300 MHz) of (TPP)Fe^{III}CH$_2$CH$_2$CH$_3$ in benzene-d_6 at 23 °C: (A) Spectrum of (TPP)Fe^{III}CH$_2$CH$_2$CH$_3$ alone; (B) spectrum after addition of 0.4 equiv of KHB(*i*-Bu)$_3$; (C) spectrum after addition of 0.7 equiv of KHB(*i*-Bu)$_3$; (D) spectrum after addition of 1.6 equiv of KHB(*i*-Bu)$_3$. Resonances are assigned as pyrr for pyrrole protons and β for the β-methylene of axial *n*-propyl group.

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[1] Clark, D. A.; Dolphin, D.; Grigg, R.; Johnson, A. W.; Pinnock, H. A. *J. Chem. Soc. C* **1968**, 881.

[2] Lexa, D.; Mispelter, J.; Saveant, J.-M. *J. Am. Chem. Soc.* **1981**, *103*, 6806.

[3] Cocolios, P.; Laviron, E.; Guilard, R. *J. Organomet. Chem.* **1982**, *228*, C39.

[4] Cocolios, P.; Lagrange, G.; Guilard, R. *J. Organomet. Chem.* **1983**, *253*, 65.

[5] Floriani, C.; Calderazzo, F. *J. Chem. Soc. A* **1971**, 3665.

[6] Tabard, A.; Cocolios, P.; Lagrange, G.; Gerardin, R.; Hubsch, J.; Lecomte, C.; Zarembowitch, J.; Guilard, R. *Inorg. Chem.* **1988**, *27*, 110.

[7] Gueutin, C.; Lexa, D.; Savéant, J.-M.; Wang, D.-L. *Organometallics* **1989**, *8*, 1607.

[8] Arasasingham, R. D.; Balch, A. L.; Cornman, C. R.; Latos-Grażynński, L. *J. Am. Chem. Soc.* **1989**, *111*, 4357.

[9] Arasasingham, R. D.; Cornman, C. R.; Balch, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 7800.

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which the Super-Hydride reagent serves as a source of an ethyl group rather than a hydride.[10,11]

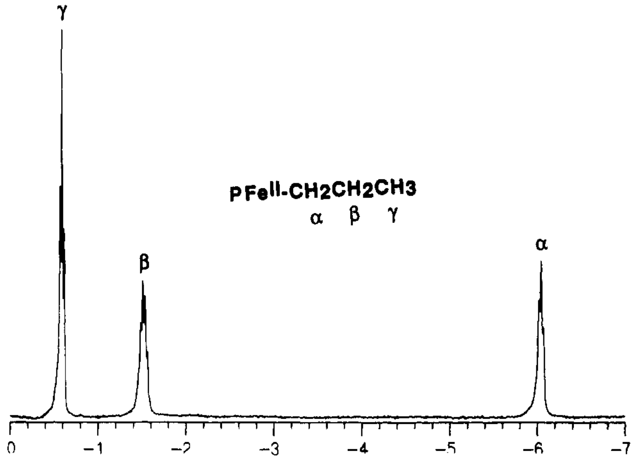
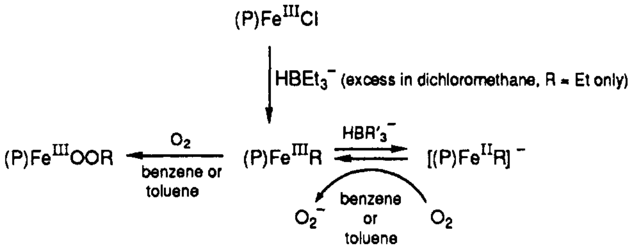


Figure 2. ^{1}H NMR spectrum (300 MHz) of (TPP)Fe^{II}CH$_2$CH$_2$CH$_3^-$ in benzene-d_6 at 23 °C resulting from addition of 1.6 equiv of KHB(i-Bu)$_3$ to (TPP)Fe^{III}CH$_2$CH$_2$CH$_3$ (expansion of trace D of Figure 1).

In dichloromethane solution, addition of further quantities of Super-Hydride does not results in reduction of the iron(III) alkyl. However, reduction to the iron(II) alkyl is observed in toluene or benzene solution. Both lithium triethylborohydride and potassium tri-*sec*-butyl borohydride (K-Selectride) are effective for this, but the solubilities of the species resulting from the use of K-Selectride are better. Figure 1 shows the effects of successive additions of K-Selectride in tetrahydrofuran solution in the dark to (TPP)Fe^{III}CH$_2$CH$_2$CH$_3$ in benzene-d_6 at 23 °C on the upfield region of the NMR spectrum, where pyrrole and axial ligand resonances are present. The solution remains homogeneous throughout the addition. Trace A shows the spectrum of the iron(III) alkyl alone with the characteristic pyrrole resonance of a low-spin iron(III) complex at −18.6 ppm and the β-methylene protons of the n-propyl ligand at −55.5 ppm.[8] On addition of successive amounts of K-Selectride the pyrrole resonance and the methylene resonance broaden and move to lower field. Addition of an excess of the reducing agent is necessary to effect the complete reduction that is seen in trace D. An expansion of that spectrum is shown in Figure 2. The three resonances expected for a coordinated n-propyl group are present with the upfield ring-current shifts that are characteristic of diamagnetic metalloporphyrin complexes bearing axial alkyl ligands.[12] Notice that the spin–spin splittings expected for such a propyl ligand are also clearly resolved. The pyrrole resonance is found at 8.10 ppm, and the phenyl resonances of the TPP ligand occur in the 7–7.5 ppm region. Integration of the pyrrole and phenyl resonances and the axial ligand resonances indicates that one axial ligand is present in the iron(II) complex. There is no evidence for the formation of other iron prophyrins during this reduction. These spectral characteristics indicate that the iron(II) alkyl complex is diamagnetic, in contrast with the paramagnetic (S = 2) state found for other anionic iron(II) porphyrin complexes with chloride, alkoxide, phenoxide, or acetate ion as axial ligands.[13] Since the reducing agent is added as a solution in tetrahydrofuran, it is likely that the iron(II) alkyl complex has an axial tetrahydrofuran ligand. The broad resonances seen in traces B and C of Figure 1, then, result from rapid electron exchange between the paramagnetic (P)Fe^{III}CH$_2$CH$_2$CH$_3$ and the diamagnetic [(P)Fe^{II}CH$_2$CH$_2$CH$_3$]$^-$. The resonance positions are a population-weighted average of the two forms. Reduction of (TPP)Fe^{III}CH$_2$CH$_3$ follows a similar course and results in the formation of [(TPP)Fe^{II}CH$_2$CH$_3$]$^-$ with ethyl resonances at −2.25 ppm (methyl) and −6.19 ppm (methylene).

Scheme I



Addition of successive aliquots of dioxygen to a sample of [(TPP)Fe^{II}CH$_2$CH$_2$CH$_3$]$^-$ results in reversal of the process shown in Figure 1. That is, the resonances of the iron complex are broadened and the pyrrole and β-methylene resonances shift upfield until they reach the positions characteristic of (TPP)Fe^{III}CH$_2$CH$_2$CH$_3$. Only after oxidation to the iron(III) state does dioxygen insertion into the Fe–C bond occur. The result is the conversion of (TPP)FeCH$_2$CH$_2$CH$_3$ to (TPP)Fe^{III}OFe^{III}(TPP) and propionaldehyde.[8]

These observations indicate that the iron(II) alkyls can be observed directly in solution and are stable for at least 1 week in solution when protected from oxidants and light. Their low chemical and thermal stability makes them unlikely candidates for isolation in pure form. They are diamagnetic. Structurally they may resemble the analogous alkyliron(II) phthalocyanines that have recently been characterized.[14] Dioxygen serves to oxidize the iron(II) form to the iron(III) form with subsequent insertion into the Fe^{III}–C bond. The chemical transformations are summarized in Scheme I.

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(10) Other cases of ethyl transfer from Super-Hydride are reported in: Gysling, H. J.; Luss, H. R. *Organometallics* **1989**, *8*, 363.

(11) (TAP)Fe^{III}CH$_2$CH$_3$ was the only product formed when we attempted to repeat the preparation of (TAP)Fe^{III}SH by adding (TAP)Fe^{III}Cl to the reagent obtained by mixing 1 equiv of sulfur with 2 equiv of LiHBEt$_3$ according to the reported procedure: English, D. R.; Hendrickson, D. N.; Suslick, K. S.; Eigenbrot, C. W., Jr.; Scheidt, W. R. *J. Am. Chem. Soc.* **1984**, *106*, 7258.

(12) Maskasky, J. E.; Kenney, M. E. *J. Am. Chem. Soc.* **1973**, *95*, 1443.

(13) Schappacher, M.; Ricard, L.; Weiss, R.; Montiel-Montoya, R.; Gonser, U.; Bill, E.; Trautwein, A. *Inorg. Chim. Acta* **1983**, *78*, L9–L12. Silver, J.; Lukas, B. *Inorg. Chim. Acta* **1983**, *80*, 107–113. Silver, J.; Lukas, B.; Al-Jaff, G. *Inorg. Chim. Acta* **1984**, *91*, 125. Trautwein, A.; Bill, E.; Nasri, H.; Fischer, J.; Weiss, R. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 322. Nasri, H.; Fischer, J.; Weiss, R.; Bill, E.; Trautwein, A. *J. Am. Chem. Soc.* **1987**, *109*, 2549.

(14) Tahiri, M.; Doppelt, P.; Fischer, J.; Weiss, R. *Inorg. Chem.* **1988**, *27*, 2897.

(15) Abbreviations: P, porphyrin dianion; TPP, *meso*-tetraphenylporphyrin dianion; TAP, tetrakis(p-methoxyphenyl)porphyrin dianion; R, alkyl group or hydrogens.