$(CH_3)_3N·HCl$ and $NaBH_3CN$. The amine-exchange reactions were carried out in 250-mL glass pressure reaction vessels. The pressure reaction vessels and their safety shields were purchased from Lab-Crest Scientific Co., Warminster, PA. Although the NH_3 exchange has been carried out in the glass vessel without incident, the use of stainless-steel vessels is greatly preferred for safety.

Trimethylamine–(Ethylcarbamoyl)borane (1).[3,4] A solution of trimethylamine–cyanoborane (11.9 g, 0.12 mol) and 250 mL of 1 M Et_3OBF_4 in CH_2Cl_2 (0.25 mol) was refluxed under nitrogen for 24 h. The reaction mixture was cooled to 0 °C, and 1 N NaOH was added slowly with vigorous stirring until the solution was basic (pH ~8). After the mixture was stirred for 1 h at room temperature, the organic layer was separated and the aqueous layer was extracted three times with CH_2Cl_2. The organic portions were combined and dried over $MgSO_4$, and the solvent was removed in vacuo. The remaining viscous liquid was distilled under vacuum with minimum heating to give **1**: 13.1 g (75%); bp 80 °C (0.15 torr); IR (neat) 3289 (ν(NH)), 2915 (ν (CH)), 2330 (ν(B–H)), 1590 (amide I), 1480 (amide II) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07 (t, CH_3CH_2), 2.75 (s, CH_3N), 3.57 (m, CH_2CH_3), 5.43 (br s, NH); ^{13}C NMR ($CDCl_3$) δ 15.3 (CH_3CH_2), 31.5 (CH_2CH_3), 51.8 (CH_3N), 182.8 (CO); ^{11}B NMR ($CDCl_3$, $BF_3·Et_2O$) δ −7.4 (1:2:1 t, J_{BH} = 90 Hz). Anal. Calcd for $C_6H_{17}BN_2O$: C, 50.10; H, 11.83; N, 19.49; B, 7.45. Found: C, 49.86; H, 11.69; N, 19.59; B, 7.50.

Dimethylamine–(Ethylcarbamoyl)borane (2). Anhydrous $(CH_3)_2NH$ (50 g, 1.1 mol) was cooled to 0 °C and poured into the glass pressure vessel containing **1** (14.38 g, 0.1 mol) kept at 0 °C. The vessel was assembled and kept at room temperature for 8 $^1/_2$ days with occasional shaking each day. The reaction vessel was then cooled to 0 °C and slowly opened. To this solution was added ca. 80 mL of pentane, and the volatile amines were allowed to evaporate off. The remaining amines and solvent were removed by rotary evaporation. A pale yellow liquid was obtained that had ca. 21% unreacted **1** (by proton NMR). The mixture was taken up in CH_2Cl_2 and washed once with water. The water washing was repeatedly extracted with CH_2Cl_2, and the proton NMR spectrum of the CH_2Cl_2 extracts showed that it contained only the starting amide (**1**). The CH_2Cl_2 solution containing the product, uncontaminated by **1** (by proton NMR), was dried over $MgSO_4$ and treated with charcoal. The solvent was then removed by rotary evaporation and the pale yellow oil (**2**) (10.1 g (77.7%)) was vacuum distilled: bp 110–112 °C (0.2 torr); IR (CH_2Cl_2) 3440 (ν(NH)), 2965 (ν(CH)), 2365 (ν(BH)), 1590 (amide I), 1490 (amide II) cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.06 (t, CH_3CH_2), 2.40 (d, CH_3N), 3.18 (m, CH_2CH_3), 5.80 (br s, amine H), 6.45 (br s, amide H); ^{11}B NMR ($CDCl_3$, $BF_3·Et_2O$) δ −11.55 (t, J_{B-H} = 88 Hz); ^{13}C NMR ($CDCl_3$) δ 15.26 (CH_3CH_2), 32.33 (CH_2CH_3), 42.91 (CH_3N). Anal. Calcd for $C_5H_{15}BN_2O$: C, 46.20; H, 11.63; N, 21.55. Found: C, 45.94; H, 11.58; N, 21.30.

Methylamine–(Ethylcarbamoyl)borane (3). Anhydrous methylamine was condensed (ca. 30 mL) at −78 °C from the gas cylinder and transferred to the glass pressure reaction vessel containing 2.86 g (19.85 mmol) of **1** already cooled to −78 °C. The pressure reaction vessel was then assembled and slowly allowed to warm to room temperature and kept for 1 week with occasional shaking. The reaction vessel was then cooled to −78 °C and carefully opened. To this solution was added ca. 100 mL of pentane, and excess amines were allowed to evaporate off at room temperature. Some solid product separated, and the remaining solvent and was removed by rotary evaporation. The crude product was dissolved in CH_2Cl_2 (ca. 200 mL) and filtered into *n*-pentane. An off-white solid (0.92 g) separated. To the filtrate was added additional pentane, and 0.57 g of more product was obtained. The combined solid (**3**) (1.49 g (65%)) was recrystallized from CH_2Cl_2/pentane: mp 99–100 °C; IR (Nujol) 3330 (ν(NH)), 3120 (ν(CH)), 2380 (ν(BH)), 1620 (amide), 1570 (m, amide) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.09 (t, CH_3CH_2), 2.43 (t, MeN), 3.23 (m, CH_2CH_3), 4.95 (br s, amine H), 5.69 (br s, amide H); ^{13}C NMR ($CDCl_3$) δ 15.20 (CH_3CH_2), 32.30 (CH_2CH_3), 32.36 (Me_3N); ^{11}B NMR ($CDCl_3$, $BF_3·Et_2O$) δ −15.37 (t, J_{BH} = 84 Hz). Anal. Calcd for $C_4H_{13}N_2BO$: C, 41.43; H, 11.30; N, 24.16. Found: C, 41.20; H, 11.07; N, 24.03.

Ammonia–(Ethylcarbamoyl)borane (4). Anhydrous NH_3 was condensed at −78 °C from the gas cylinder and ca. 40 mL of liquid NH_3 transferred to the glass pressure reaction vessel containing 1.48 g (10.20 mmol) of **1** that was previously cooled to −78 °C. The reaction vessel was then assembled, allowed to warm to room temperature, and kept for 1 week with occasional shaking each day. The reaction vessel was then cooled to −78 °C and slowly opened. The excess NH_3 and amines were allowed to evaporate off at room temperature, ca. 200 mL of CH_2Cl_2 was added to the vessel, and the resultant mixture was filtered. The solution was kept in the refrigerator, and fluffy crystals formed. The crude product was recrystallized from doubly distilled water. The white needles (**4**) (0.62 g (60%) mp 125–126 °C) had the following spectral properties: IR (Nujol) 3350 (ν(NH)), 3270 (ν(CH)), 2340 (ν(BH)), 1620 (amide I), 1550 (amide II) cm^{-1}; ^1H NMR (D_2O) δ 1.06 (t, CH_3CH_2), 3.15 (q, CH_2CH_3); ^{13}C NMR (D_2O) δ 16.60 (CH_3CH_2), 35.22 (CH_2CH_3); ^{11}B NMR (D_2O, $BF_3·Et_2O$) δ–19.59 (t, J_{BH} = 80 Hz). Anal. Calcd for $C_3H_{11}N_2BO$: C, 35.35; H, 10.88; N, 27.48. Found: C, 35.32; H, 10.86; N, 27.72.

Acknowledgment. We thank the Army Research Office for support of this work.

Registry No. 1, 60788-35-4; **2**, 88915-69-9; **3**, 88915-70-2; **4**, 88915-71-3.

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EPR Studies of the Formation of Low-Spin Dimethoxo(tetraphenylporphinato)ferrate(III) in Solution

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Received September 19, 1983

The interaction of heme iron with its ligands has been the subject of continuing spectroscopic investigations. In particular, axial ligations in low-spin Fe(III) heme complexes have been studied most extensively by EPR spectroscopy, and various types of axial ligation modes are identified and characterized.[1,2] However, there seems to be no report on the low-spin complex in which O-donor ligands are coordinated to both the fifth and sixth axial positions. It is often tacitly supposed that the axial ligation mode O–Fe–O results in high-spin complexes because of the rather weak field nature of O-donor ligands.

In the present work, we have found, contrary to the above supposition, that the low-spin state can be effected in dimethoxo(tetraphenylporphinato)ferrate(III), $Fe(TPP)(OMe)_2^-$, which forms upon mixing of Fe(TPP)Cl with excess methoxide anion, MeO^-, in toluene–methanol. This note will report the first demonstration of the axial ligation mode O–Fe–O in low-spin Fe(III) heme complexes together with EPR characteristics obtained for $Fe(TPP)(OMe)_2^-$.

Experimental Section

Sodium methoxide (NaOMe, ~28% in methanol) was purchased from Wako Chemicals and used as obtained or by dilution with methanol. The concentration of MeO^- in methanol was determined by titration with hydrochloric acid after dilution with excess water. Toluene was purified by distillation from calcium hydride and stored over 4A molecular sieves. Methanol (Spectroquality, Dojin Chemicals) was used without further purification. Fe(TPP)Cl was synthesized and purified following published methods.[3-5]

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Table I. Comparison of the Axial Ligation Modes O–Fe–O and S–Fe–S

axial ligation mode	complex species	obsd *g* values			crystal field parameters				ref
		g_x	g_y	g_z	δ^a	μ^a	R^b	k	
O^-–Fe–O^-	$Fe(TPP)(OMe)_2^-$	1.914	2.165	2.494	8.85	4.43	0.501	1.096	this work
	$Fe(PPIXDBE)(OC_6H_4\text{-}4\text{-}NO_2)_2^-$		high spin						13
S^-–Fe–S^-	$Fe(PPIXDME)(S\text{-}n\text{-}Bu)_2^-$	1.958	2.229	2.309	6.43	7.84	1.220	1.200	16
	$Fe(PPIXDME)(SC_6H_4\text{-}4\text{-}NO_2)_2^-$	1.925	2.274	2.405	5.32	5.79	1.090	1.171	16

[a] In units of ζ (spin-orbit coupling constant, $\zeta \simeq 400$ cm^{-1}). [b] $R = \mu/\delta$.

Fe(TPP)(OMe) was prepared by combining Fe(TPP)Cl (150 mg) and excess of NaOMe (~28% in methanol; 1 mL) in benzene–methanol (5:2 v/v; 70 mL), stirring the solution for 1 h at room temperature, and reducing to a small volume under reduced pressure. The black-purple crystals that resulted were collected by filtration, washed with methanol, and dried under vacuum. Anal. Calcd for $C_{45}H_{31}N_4OFe$: C, 77.26; H, 4.47; N, 8.01. Found: C, 76.87; H, 4.55; N, 7.84.[6]

The sample for EPR measurement was prepared by adding MeO^- to Fe(TPP)Cl (or Fe(TPP)(OMe)) in toluene–methanol at room temperature. The solution was transferred into a quartz tube (4.0 mm i.d.) and frozen to glass at 77 K within a few minutes to avoid autoreduction and subsequent reoxidation by air.

EPR spectra were recorded at 77 K or below with a JEOL FE3AX spectrometer with 100-kHz field modulation. The magnetic field was measured by proton resonance, and the microwave frequency was calibrated by using DPPH as a standard ($g = 2.0036$). The *g* values were determined at the peak (or trough) and at the middle point of the first-derivative spectrum. Temperatures below 77 K were attained with a Heli-tran variable-temperature system (LTD-3-110, Air Products).

Results and Discussion

Formation of $Fe(TPP)(OMe)_2^-$ in Toluene–Methanol. Typical EPR spectra observed in toluene–methanol (5:2 v/v) at 25 K are shown in Figure 1. Three spectrally distinct complex species are found when MeO^- concentration is successively increased. The low-spin species may be assigned to the previously unidentified complex $Fe(TPP)(OMe)_2^-$, which is formed according to

$$Fe(TPP)Cl + MeO^- = Fe(TPP)(OMe) + Cl^- \quad (1)$$

$$Fe(TPP)(OMe) + MeO^- = Fe(TPP)(OMe)_2^- \quad (2)$$

Weakly interacting solvent molecules are neglected in these equations.[7] Similar spectral changes were observed at 77 K or intermediate temperatures. The spectra showed the general trend of line width broadening toward higher temperatures but with almost constant *g* values.

Reaction 2 was confirmed by using Fe(TPP)(OMe) in place of Fe(TPP)Cl as starting material. Additions of varying amount of MeO^- to Fe(TPP)(OMe) in toluene–methanol (5:2 v/v) actually yielded spectra at $[MeO^-]_0/[Fe(TPP)(OMe)]_0 = 1$, 9, and ~50 that were quite similar in both *g* values and relative intensities to those shown in parts b, c, and d, respectively, of Figure 1. The complete conversion of Fe(TPP)(OMe) to $Fe(TPP)(OMe)_2^-$ was not observed even with a larger excess of MeO^- added. Further, no visible spectral changes were detected at room temperature on mixing of Fe(TPP)(OMe) with MeO^-. It appears that reaction 2 is exothermic and $Fe(TPP)(OMe)_2^-$ is formed and stabilized only at lower temperature. The equilibrium constant K_2 for reaction 2 is poorly defined from the present results. However, all the observations mentioned above are consistent with the view that K_2 is very small and that stepwise binding of MeO^- to iron takes place with much larger difficulty in reaction 2 than in reaction 1. This feature of the axial ligation process affords a sharp contrast to the one found in other low-spin heme complexes such as $Fe(TPP)(Im)_2^+$ [8] and $Fe(PPIX)(CN)_2^-$.[9]

The solvent composition showed a marked effect: The formation of $Fe(TPP)(OMe)_2^-$ decreased with the decreasing content of methanol in the solvent and was not detected when the methanol to toluene ratio was less than 1:50 (v/v). The decreasing solvent polarity is likely to lower the stability of the anionic species $Fe(TPP)(OMe)_2^-$. The *g* values were independent of the solvent composition, indicating that a single low-spin species is present in toluene–methanol. Attempts to isolate and characterize the low-spin complex $Fe(TPP)(OMe)_2^-$ as a crystalline solid have so far been unsuccessful irrespective of many solvent systems and crystallization methods employed.

Axial Ligation Mode O–Fe–O. Low-spin Fe(III) heme complexes can be classified into several types according to their axial ligation mode X–Fe–Y, where X and Y represent neutral or anionic donor atoms of axial ligands. There are six types of axial ligation modes in total, when the axial ligand is limited to N-, O-, and S-donor ligands. Of these, five types (N–Fe–N, N–Fe–O, N–Fe–S, O–Fe–S, and S–Fe–S) have so far been identified and characterized. The *g* values and crystal field parameters characteristic of each type have been summarized in a table by Holm et al.[1] and in the crystal field correlation diagram by Blumberg et al.[10]

The present work provides the first demonstration of the remaining axial ligation mode O–Fe–O in low-spin Fe(III) heme complexes. This ligation mode usually results in a high-spin ground state, as is evidenced by the recent studies on $Fe(TPP)(H_2O)_2^+$,[11] $Fe(TPP)(Me_2SO)_2^+$,[12] and $Fe(PPIXDBE)(OC_6H_4\text{-}4\text{-}NO_2)_2^-$.[13] The low-spin ground state, which is effected in $Fe(TPP)(OMe)_2^-$, is attributable to a larger ligand field strength of MeO^- compared with other O-donor ligands. In fact, it is known that the σ-donor strength increases in the order $H_2O \sim Me_2SO < PhO^- < MeO^-$.[14]

The *g* values for $Fe(TPP)(OMe)_2^-$ were analyzed with the assumption of a pure t_2^5 electron configuration as described previously.[15] The crystal field parameters obtained are given

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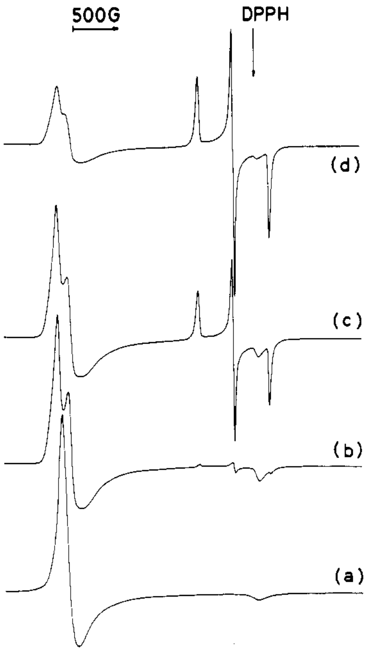

Figure 1. EPR spectra at 25 K of Fe(TPP)Cl in toluene–methanol (5:2 v/v) in the absence or presence of the MeO^- anion: $[Fe(TPP)Cl]_0 = 1.4 \times 10^{-3}$ M, $[MeO^-]_0/[Fe(TPP)Cl]_0 = 0$ (a), 2 (b), 10 (c), and $\sim$50 (d). The spectra indicate three complex species in the solutions. They are assigned to Fe(TPP)Cl (high spin; $g_x = g_y = 6.03$, $g_z = 2.00$), Fe(TPP)(OMe) (high spin; $g_x = 5.55$, $g_y = 6.40$, $g_z = 1.99$), and $Fe(TPP)(OMe)_2^-$ (low spin; $g_x = 1.914$, $g_y = 2.165$, $g_z = 2.494$) with the spin state and g values in parentheses.

in Table I. The tetragonal and rhombic splittings in the three t_2 orbitals, δ and μ, respectively, the crystal field rhombicity R, and the orbital reduction factor k fall within the parameter ranges allowable for the analysis based on the pure t_2^5 configuration, indicating that $Fe(TPP)(OMe)_2^-$ is unambiguously in the low-spin ground state.

In Table I are listed, for comparative purpose, the crystal field parameters for the corresponding complexes with axial ligation mode S–Fe–S, $Fe(PPIXDME)(S\text{-}n\text{-}Bu)_2^-$ and $Fe(PPIXDME)(SC_6H_4\text{-}4\text{-}NO_2)_2^-$.[16] It is generally accepted that the anionic O-donor ligands RO^- and PhO^- are weaker in ligand field strength than the corresponding thiolates RS^- and PhS^-, which manifests itself in the difference in spin states between $Fe(PPIXDBE)(OC_6H_4\text{-}4\text{-}NO_2)_2^-$ and $Fe(PPIXDME)(SC_6H_4\text{-}4\text{-}NO_2)_2^-$. In view of this, the greater δ value for $Fe(TPP)(OMe)_2^-$ compared with $Fe(PPIXDME)(S\text{-}n\text{-}Bu)_2^-$ is at first sight somewhat surprising. However, such apparent discrepancy may be removed, if we remember that the spin state is determined mainly by metal–ligand σ bonding, while δ and μ are affected by π bonding.[17] It seems that the axial ligation mode O–Fe–O gives the largest δ value among the six types of axial ligation modes.[1,10] The smaller μ and R values are consistent with the trend in crystal field rhombicity (E/D) found in five-coordinate high-spin Fe(III) porphyrin complexes with RO^-, PhO^-, and PhS^- as axial ligands.[1,13,18]

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Further Examples of Binuclear Phosphido-Bridged Complexes of Rhodium(I). Evidence for Bridge-Cleavage Reactions

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Received June 28, 1983

Meek and co-workers[1-4] have reported the preparation and properties of several diphenylphosphido-bridged polynuclear complexes of Rh. During the course of our studies of *heteronuclear* phosphido-bridged complexes of Rh,[5-8] we also had the occasion to prepare and examine several new *homonuclear* phosphido-bridged Rh complexes that complement those described by Meek and Kreter.[3,4] These workers prepared $[Rh_2(\mu\text{-}PPh_2)_2(COD)_2]$ (**1**) (COD = 1,5-cyclooctadiene) by reaction 1 and extensively studied its derivative chemistry.

$$[Rh_2(\mu\text{-}Cl)_2(COD)_2] + 2LiPPh_2 \rightarrow \underset{\mathbf{1}}{[Rh_2(\mu\text{-}PPh_2)_2(COD)_2]} + 2LiCl \quad (1)$$

They showed that both COD ligands of **1** can be replaced by chelating diphosphine ligands but that only one COD can be substituted by tertiary phosphines under normal thermal conditions.

We show herein that LiPMePh works equally well in these syntheses, that *mono*(phosphido)-bridged complexes can be easily prepared by control of the reaction stoichiometry of eq 1, and that monodentate phosphines can indeed replace both COD ligands when the substitution reactions are carried out under an H_2 atmosphere. We also describe results which demonstrate that reversible dissociation of these binuclear complexes into mononuclear fragments must occur during the course of some of their reactions.

Experimental Section

$[Rh_2(\mu\text{-}Cl)_2(COD)_2]$,[9] $LiPPh_2$,[10] LiPMePh,[10] and $[Rh_2(\mu\text{-}PPh_2)_2(COD)_2]$[3] were prepared according to literature procedures. PPh_2H, PMePhH, PEt_3 (Strem Chemical Co.), and 1,5-cyclooctadiene (Aldrich Chemical Co.) were obtained commercially. Solvents and liquid chemicals were dried by standard methods, and all reactions were carried out under a prepurified N_2 atmosphere by using standard Schlenk techniques.[11] All reported ^{31}P NMR chemical shifts are relative to external H_3PO_4 with downfield shifts positive. The ^{31}P NMR spectrum of $[Rh_2(\mu\text{-}PPh_2)_2(PEt_3)_4]$ was simulated so external to extract accurate coupling constants by using the program "Parameter Adjustment in NMR by Iteration Calculation" (PANIC), an Aspect 2000 NMR software package. Elemental analyses were obtained by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

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