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Transition Metal-Mediated Carbon Insertion Reaction of *arachno*-6,8-$C_2B_7H_{13}$: Synthesis and Characterization of *nido*-6-R-5,6,9-$C_3B_7H_{10}$

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We previously reported our results concerning the metal-mediated alkylation reaction of a boron hydride, in which Fischer-type carbene complexes were found to promote the conversion of *arachno*-$S_2B_7H_8^-$ to the alkylated cage compound, *arachno*-4-RCH2-6,8-$S_2B_7H_8$ as shown in equation 1 and 2.[1]

$$S_2B_7H_8^- + (CO)_5M\{=C(OCH_3)R\} \rightarrow [(CO)_5M\{C(OCH_3)(R)(S_2B_7H_8)\}]^- \quad (1)$$

$$[(CO)_5M\{C(OCH_3)(R)(S_2B_7H_8)\}]^- + H^+ \rightarrow arachno\text{-}4\text{-}RCH_2\text{-}6,8\text{-}S_2B_7H_8 \quad (2)$$

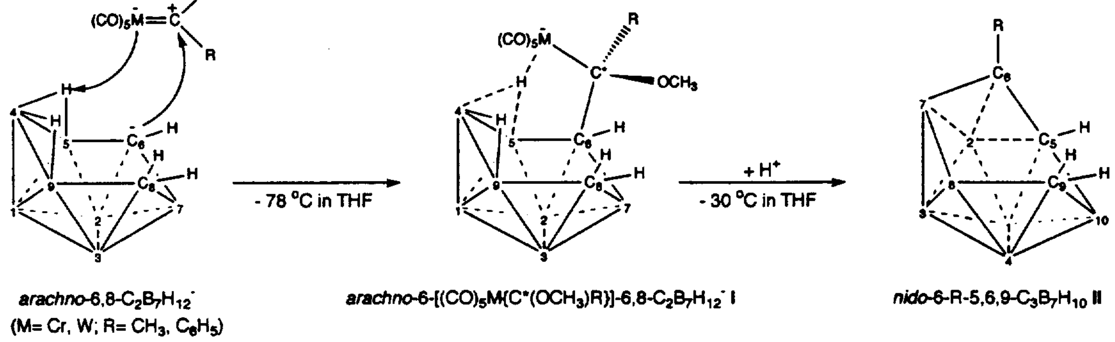
$$(M=Cr,\ W;\ R=CH_3,\ C_6H_5)$$

The result of the foregoing reactions suggests that isoelectronic *arachno*-$C_2B_7H_{12}^-$ anion might also attack Fischer-type carbene complexes. Consequently, we have found that *arachno*-$C_2B_7H_{12}^-$ anion readily reacted with Fischer-type carbene complexes[2] at room temperature. But, in contrast to the reactions with *arachno*-$S_2B_7H_8^-$, carbene-carbon insertion into the cage results in the production of new tricarbon carborane *nido*-6-R-5,6,9-$C_3B_7H_{10}$ (**IIa**: R=CH_3; **IIb**: R=C_6H_5) in good yields.

The reaction of *arachno*-6,8-$C_2B_7H_{13}$ with NaH in THF at room temperature produces a paint yellow solution of *arachno*-$C_2B_7H_{12}^-$. This anion was treated with (methoxy)(alkyl) metal carbene complexes for 6 h, producing the anionic complexes I (Scheme 1). After removing the solvent *in vacuum*, the residue was diluted in dry dichloromethane and treated with the anhydrous hydrogen chloride at −78 ℃. The reaction mixture was stirred for 1 h at −10 ℃, affording after workup (see experimental section) and purification the tricarbon carborane complex **II**.

The compound **IIa** was first prepared *via* thermal reaction of nitriles with *arachno*-$Na^+C_2B_7H_{12}^-$ in 35% yield.[3,4] The reaction required at least 2 weeks to reach completion in refluxing nitrile solution. It was found that our synthesis allow routine production of **IIa** in yields of 50% or better at room temperature and shortened the reaction time dramatically to 6 h-14 h. Thus, a more efficient procedure for production of **IIa** was developed.

Exact mass measurement and elemental analysis support the proposed composition of *nido*-6-C_6H_5-5,6,9-$C_3B_7H_{10}$ **IIb**. The ^{11}B spectrum of **IIb** (Figure 1b) is also consistent with the proposed cage skeleton, showing seven different doublets of intensity 1, with the peak at −1.2 ppm having a narrow line width characteristic of a boron (B10) located between two heteroatoms (C5 and C9). The assignment of these resonances to the B8, B7, B10, B1, B2, B3, and B4 borons, respectively, (as shown in Scheme 1) is consistent with the assign-



Scheme 1.

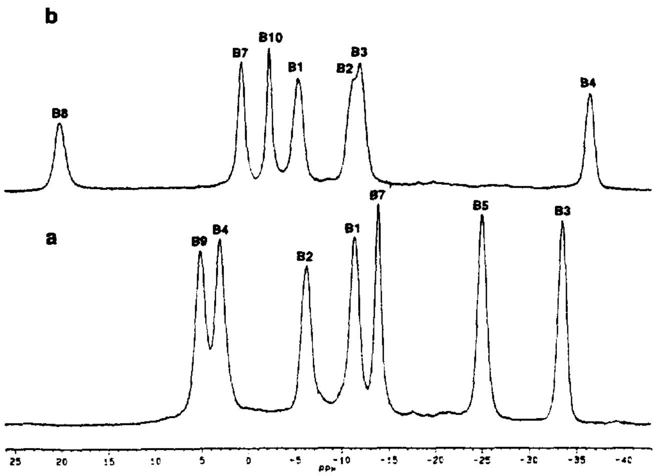


Figure 1. The 64.2 MHz $^{11}B\{^1H\}$ NMR spectra of **Ia** (a) and **IIb** (b).

ments previously made by Sneddon for the spectrum of **IIa**.[3~6] Furthermore ^{11}B-^{11}B COSY 2D NMR spectra show all the expected cross peaks between adjacent borons. The $^{13}C\{^1H\}$ NMR spectrum of complex **IIb** is likewise in agreement with the proposed cage structure and confirms the presence of a CH_2 group at the cage 9-position. The ^1H NMR spectrum of **IIb** contains one phenyl and three cage CH resonances. The peak at -1.8 ppm is assigned to the 6-CHendo proton on the basis of the similarity of its chemical shift to the high-field shifts normally observed for the endo-proton resonances in complex **IIa**. The data further indicate that **IIb** is a same cage system of the *nido*-6-CH_3-5,6,9-$C_3B_7H_{10}$ carborane recently reported by the Sneddon group.[3~6] Thus, the specroscopic data discussed above support the formation of **II** as a 10-vertex tricarbon carborane formed by one-carbon insertion reaction of Fischer-type carbene complexes.

The reaction was fast, only requiring 6 h-14 h at room temperature to reach completion. Therefore, the formation of complex **II** suggests the following reaction route is involved as shown in equation 3 and 4.

$$\begin{aligned}&\textit{arachno}\text{-Na}^+C_2B_7H_{12}^- + (CO)_5M\{=C(OCH_3)R\}\\&(M=Cr,\ W;\ R=CH_3,\ C_6H_5) \rightarrow\\&\textit{arachno}\text{-Na}^+[(CO)_5M\{C(OCH_3)(R)(C_2B_7H_{12})\}]^-\ \text{I} \qquad (3)\end{aligned}$$

$$\begin{aligned}&\textit{arachno}\text{-Na}^+[(CO)_5M\{C(OCH_3)(R)(C_2B_7H_{12})\}]^-\ \text{I} + HCl \rightarrow\\&\textit{nido}\text{-6-R-5,6,9-}C_3B_7H_{10}\ \text{II} + NaCl + CH_3OH + M(CO)_6 + H_2 \qquad (4)\end{aligned}$$

The reaction was found to proceed at -20 ℃ to give the unstable metallacarbaborane intermediate I. These compounds can be obtained quantitatively in all reactions described above but decompose slowly in solution above -10 ℃. The new compounds would be *arachno*-$Na^+[(CO)_5M\{C(OCH_3)(R)(C_2B_7H_{12})\}]^-$ (**Ia**: $R=CH_3$, $M=Cr$; **Ib**: $R=C_6H_5$, $M=Cr$) supported by ^{11}B NMR data. The ^{11}B-NMR spectrum of **Ia**, shown in Figure 1a, shows seven resonances of equal intensity. The extremely complex and broad ^1H NMR spectrum (25 ℃) precludes structural assignment for **Ia**. However, broad high field absorption observed at -12 ppm may indicate the presence of the metal hydride complex. Such metal hydride intermediates had been observed in the reaction of *arachno*-$S_2B_7H_8^-$ with Fischer-type carbene complexes as shown in equation 1.[1] Thus, the proposed structure for complex **I** is a substituted *arachno*-6,8-$C_2B_7H_{13}$ system in which the carbene carbon is directly attached to the 6-position cage carbon atom.

A possible reaction sequence leading to the formation of **II** is shown in Scheme 1. Previous studies have shown that in *arachno*-$C_2B_7H_{12}^-$ the negative charge is localized on the carbon site.[7] Nucleophilic attack of the anion at the carbene carbon should then generate a product (as is observed for **II**) having one of the original cage carbons and the carbene carbon in adjacent positions. Thus, reaction of the anion with the Fischer-type carbene complex would create a metallacarbaborane intermediate **I**; consequently, in the carborane there are two additional hydrogens present and complete reduction to both methanol and metal carbonyl ($M(CO)_6$) is possible in the presence of acid. This reductive cleavage[8] then allows the incorporation of the carbene carbon into the cage. This proposed reaction sequence is speculative and additional detailed studies will be required before an exact reaction mechanism can be confirmed; however, it is clear that the intermediate **I** appears to play a unique role in each of the reactions discussed above.

Thus, we provide an efficient synthetic route to the *nido*-6-R-5,6,9-$C_3B_7H_{10}$ **II** tricarbon carborane system. These results suggest that nucleophilic *arachno*-$C_2B_7H_{12}^-$ may be able to attack other polarized metal-carbon bonds, providing a new synthetic route to multi-carbon carborane clusters. We are continuing to study both the scope of these reactions and the chemistry of these unique tricarbon carborane clusters.

Experimental

All Manipulation were carried out using standard high-vacuum or inert-atmosphere techniques described by Shriver.[9]

Methods and Materials. *arachno*-6,8-$C_2B_7H_{13}$ was prepared as reported previously.[10] Oil-dispersed sodium hydride was obtained from Aldrich and was washed with hexane under a nitrogen atmosphere prior to use. The $(CO)_5Cr\{=C(OCH_3)(CH_3)\}$,[2b] $(CO)_5Cr\{=C(OCH_3)(C_6H_5)\}$,[2c] $(CO)_5W\{=C(OCH_3)(CH_3)\}$,[2b] and $(CO)_5W\{=C(OCH_3)(C_6H_5)\}$[2b] were prepared according to the literature methods. The majority of solvents were of reagent grade and were used without further purification. Tetrahydrofuran was freshly distilled from sodium-benzophenone and methylene chloride was dried over calcium chloride. Anhydrous hydrogen chloride (HCl/Et_2O) and all other reagents were commercially obtained, as indicated, and used as received. Analytical thin-layer chromatography was conducted on 0.25 mm (5×10 cm) silica gel F-254 plates (Merck). Flash column chromatography was performed with silica gel (230-400 mesh, EM Science). Silica gel was obtained from J. T. Baker Co. and was dried before use. All reactions involving dicarbaborane anion were carried out under nitrogen atmosphere.

Physical Measurements. ^1H NMR spectra at 200 MHz and ^{11}B NMR spectra at 64.2 MHz were obtained on a Bruker AM-200 Fourier transform spectrometer. All boron-11 chemical shifts were referenced to $BF_3\cdot O(C_2H_5)_2$ (0.0 ppm) with a negative sign indicating an upfield shift. All proton chemical shifts were measured relative to internal residual benzene from the lock solvent (99.5% C_6D_6) and then referenced to Me_4Si (0.00 ppm).

Two-dimensional COSY ^{11}B-^{11}B NMR experiments[11] were conducted with s-type selection parameters at 64.2 MHz. The sweep widths in the F_2 direction was 20000 Hz and in the F_1 direction 10000 Hz and a total of 128 increments (increment size 0.05 ms) was collected, with each slice having 512w F_2 data points. The data were zero-filled twice in the F_1 directions and subjected to 2D Fourier transformation with sine-bell apodization in both domains. A total of 128 scans for **IIb** and 256 scans for **Ia** were taken for each increment with a recycling time of 100 ms.

High- and low-resolution mass spectra were obtained on a VG Micromass 7070H mass spectrometer. All melting points were uncorrected. Elemental analyses were obtained from Schwazkopf Laboratories, Woodside, NY. Infrared spectra were obtained on a Perkin-Elmer 1430 spectrophotometer.

General Procedure for the Synthesis of *nido*-6-R-5,6,9-$C_3B_7H_{10}$ II. A 100-mL round bottom flask fitted with a vacuum stopcock was charged with *arachno*-6,8-$C_2B_7H_{13}$ (0.34 g, 3.0 mmol) and NaH (0.10 g, 4.2 mmol). Tetrahydrofuran (20 mL) was distilled *in vacuo* into the reaction flask cooled with liquid N_2, and the flask was allowed to warm to room temperature, whereupon hydrogen gas was evolved. After gas evolution ceased (1 h), the resulting yellow solution was filtered. The (methoxy)(alkyl) metal carbene complex (3.2 mmol, 1.1 equiv) in THF was added *via* canula to a flask containing a solution of $Na^+C_2B_7H_{12}^-$ at −78 ℃. The initial yellow or red solution turned to brown after the addition was concluded. The reaction mixture was stirred at −78 ℃ for 1h and for 6 h at room temperature. The solution gradually turned dark green, suggesting the formation of a metallacarbaborane complex. ^{11}B NMR spectra taken at this point confirmed the exclusive formation of the anion *arachno*-$Na^+[(CO)_5M\{C(OCH_3)(R)(C_2B_7H_{12})\}]^-$ (**Ia**: R=CH_3, M=Cr; **Ib**: R=C_6H_5, M=Cr). THF was removed *in vacuo* and the residue was dissolved in 20 mL of methylene chloride. This suspension was maintained at −78 ℃ while 5 mL of 1 M HCl in Et_2O was added. The reaction mixture was warmed to −10 ℃ and stirred for 1 h at this temperature. Subsequent separation was performed by vacuum distillation gave air sensitive complex *nido*-6-R-5,6,9-$C_3B_7H_{10}$ (**IIa**: R=CH_3; **IIb**: R=C_6H_5).

Reaction of $Na^+C_2B_7H_{12}^-$ with $(CO)_5Cr\{=C(OCH_3)(CH_3)\}$. $(CO)_5Cr\{=C(OCH_3)(CH_3)\}$ (0.80 g, 3.2 mmol) in THF (20 mL) was treated with $Na^+C_2B_7H_{12}^-$, prepared from *arachno*-6,8-$C_2B_7H_{13}$ (0.34 g, 3.0 mmol) and NaH (0.10 g, 4.2 mmol) in THF (~20 mL), according to the general procedure. After stirring the reaction mixture for 6 h at room temperature, ^{11}B NMR spectra taken at this point indicated that the starting material had been completely consumed and that *arachno*-$Na^+[(CO)_5Cr\{C(OCH_3)(CH_3)(C_2B_7H_{12})\}]^-$ anion Ia was the sole product. The intermediate complex Ia was slowly decomposed in solution at room temperature: ^{11}B NMR (64.2 MHz, ppm, tetrahydrofuran-d_8) 5.1 (d, B9, $J_{BH}=130$), 3.0 (d, B4, $J_{BH}=120$), −6.2 (d, B2, $J_{BH}=140$), −11.4 (d, B1, $J_{BH}=150$), −13.9 (d, B7, $J_{BH}=145$), −25.0 (d, B5, $J_{BH}=160$), −33.5 (d, B3, $J_{BH}=140$); 2D ^{11}B-^{11}B COSY NMR (64.2 MHz, ppm, tetrahydrofuran-d_8, ^{11}B spin-decoupled) B9-B1 (w), B4-B1 (s), B4-B5 (m), B2-B1 (s), B2-B7 (m), B2-B5 (s), B2-B3 (s), B1-B5 (s), B1-B3 (s), B7-B3 (m); ^1H NMR (200.13 MHz, ppm, tetrahydrofuran-d_8) 3.6 (br, s, OCH_3), 2.9 (br, s, CH_{exo}), 2.4 (br, s, CH_{exo}), 1.0 (br, s, CH_3), −1.5 (br, s, CH_{endo}), −2.0 (br, s, B-*H*-B), −12.0 (br, s, M*H*). Protonation followed by vacuum distillation of the resulting reaction mixture under 0.01 mmHg at room temperature gave the complex *nido*-6-CH_3-5,6,9-$C_3B_7H_{10}$ IIa (0.24 g, 1.8 mmol, 58% yield).

Reaction of $Na^+C_2B_7H_{12}^-$ with $(CO)_5W\{=C(OCH_3)(CH_3)\}$. The general procedure as described above was employed by using 3.0 mmol of $Na^+C_2B_7H_{12}^-$, except that $(CO)_5W\{=C(OCH_3)(CH_3)\}$ (1.2 g, 3.2 mmol) was used instead of $(CO)_5Cr\{=C(OCH_3)(CH_3)\}$ and that the reaction was run until completion (12 h). The completion of the reaction was monitored by ^{11}B NMR spectroscopy. After *ca.* 2 h of further stirring, green brown reaction mixture was connected to a vacuum and the solvent was evaporated. The residue was dissolved in dry CH_2Cl_2, cooled to −78 ℃ and HCl/Et_2O (5.0 mmol, 1.7 equiv) was added. Cooling bath was removed, and the heterogeneous reaction mixture was stirred for 1 h at −10 ℃. The reaction mixture was quickly filtered through an activated pad of silica gel, and the solvent was removed under vacuum. The crude residue was purified by vacuum distillation under 0.01 mmHg at room temperature gave IIa (0.20 g, 1.5 mmol, 49% yield).

Reaction of $Na^+C_2B_7H_{12}^-$ with $(CO)_5Cr\{=C(OCH_3)(C_6H_5)\}$. $(CO)_5Cr$-/7=$C(OCH_3)(C_6H_5)\}$ (1.0 g, 3.2 mmol) in THF (20 mL) was treated with $Na^+C_2B_7H_{12}^-$, prepared from *arachno*-6,8-$C_2B_7H_{13}$ (0.34 g, 3.0 mmol) and NaH (0.10 g, 4.2 mmol) in THF (20 mL), according to the general procedure. After stirring the reaction mixture for 6 h at room temperature, ^{11}B NMR spectra taken at this point indicated that the starting material had been completely consumed and that *arachno*-$Na^+[(CO)_5Cr\{C(OCH_3)(C_6H_5)(C_2B_7H_{12})\}]^-$ anion **Ib** was the sole product. The intermediate complex **Ib** was slowly decomposed in solution at room temperature: ^{11}B NMR (64.2 MHz, ppm, tetrahydrofuran-d_8) 6.6 (d, B9, $J_{BH}=125$), 4.2 (d, B4, $J_{BH}=130$), −5.0 (d, B2, $J_{BH}=135$), −10.1 (d, B1, $J_{BH}=130$), −13.3 (d, B7, $J_{BH}=135$), −23.4 (d, B5, $J_{BH}=160$), −32.0 (d, B3, $J_{BH}=145$); ^1H NMR (200.13 MHz, ppm, tetrahydrofuran-d_8) 7.6 (br, m, C_6H_5), 3.9 (br, s, OCH_3), 3.0 (br, s, CH_{exo}), 2.4 (br, s, CH_{exo}), −1.5 (br, s, CH_{endo}), −2.1 (br, s, B-*H*-B), −11.6 (br, s, M*H*). Protonation followed by sublimation of the resulting reaction mixture under 0.01 mmHg at room temperature gave the complex *nido*-6-C_6H_5-5,6,9-$C_3B_7H_{10}$ IIb (0.35 g, 1.8 mmol, 59% yield): mp 30-32 ℃ (Sublimed at room temperature); ^{11}B NMR (64.2 MHz, ppm, C_6D_6) 20.1 (d, B8, $J_{BH}=170$), 1.0 (d, B7, $J_{BH}=160$), −1.2 (d, B10, $J_{BH}=190$), −4.4(d, B1, $J_{BH}=180$), −10.3 (d, B2, $J_{BH}=110$), −11.3 (d, B3, $J_{BH}=100$), −36.5 (d, B4, $J_{BH}=160$); 2D ^{11}B-^{11}B COSY NMR (64.2 MHz, ppm, C_6D_6, ^{11}B spin-decoupled) B8-B7 (s), B8-B3 (s), B8-B4 (m), B7-B2 (w), B7-B3 (s), B10-B1 (w), B10-B4 (w), B1-B2 (s), B1-B3 (s), B1-B4 (s), B2-B3 (s), B3-B4 (s); ^1H NMR (200.13 MHz, ppm, C_6D_6) 7.4 (br, m, C_6H_5), 2.6 (s, CH_{exo}), 2.3 (s, CH_{exo}), −1.8 (br, s, CH_{endo}); ^{13}C NMR (50.3 MHz, ppm, C_6D_6, proton-decoupled): 160 (s, *C*6), 132, 130, 120 (s, C_6H_5), 62 (s, *C*5), 32 (s, *C*9); IR (KBr) 3070 (w), 3040 (w), 2600 (s), 2580 (s, sh), 1600 (m), 1500 (s), 1450 (br, m), 1380 (m, br), 1260 (w), 1230 (w), 1215 (w), 1170 (w), 1080 (w, sh), 1035 (s), 870 (w), 820 (w). Mass measurement for $^{11}B_7{}^{12}C_9{}^1H_{15}$: calcd, 200.1821; found, 200.1810. Anal.

Calcd for $B_7C_9H_{15}$: C, 54.35; H, 7.60. Found: C, 54.54; H, 7.70.

Reaction of $Na^+C_2B_7H_{12}^-$ with $(CO)_5W\{=C(OCH_3)(C_6H_5)\}$. The general procedure as described above was employed by using 3 mmol of $Na^+C_2B_7H_{12}^-$, except that $(CO)_5W\{=C(OCH_3)(C_6H_5)\}$ (1.4 g, 3.2 mmol) was used instead of $(CO)_5Cr\{=C(OCH_3)(C_6H_5)\}$ and that the reaction was run until completion (12 h). The completion of the reaction was monitored by ^{11}B NMR spectroscopy. After *ca.* 2 h of further stirring, green brown reaction mixture was connected to a vacuum and the solvent was evaporated. The residue was dissolved in dry CH_2Cl_2, cooled to -78 ℃ and HCl/Et_2O (5.0 mmole, 1.7 equiv) was added. Cooling bath was removed, and the heterogeneous reaction mixture was stirred for 1 h at -10 ℃. The reaction mixture was quickly filtered through an activated pad of silica gel, and the solvent was removed under vacuum. The crude residue was purified by sublimation under 0.01 mmHg at room temperature gave **IIb** (0.31 g, 1.6 mmol, 52% yield).

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Resonance Raman Spectra of High-Valence Fluorooxoiron Tetrakis(pentafluorophenyl)porphyrin

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The high valence oxoferryl porphyrins are often found in many heme containing enzymes as reaction intermediates in their respectable reaction cycles.[1~3] Given the diverse chemistry catalyzed by these various enzymes, the heme pocket modulation of the chemical reactivity of the $Fe^{IV}=O$ unit seems. Resonance Raman (RR) detection of the ν ($Fe^{IV}=O$) in various protein species and model compounds supports this notion.[4]

The tetrakis(pentafluorophenyl)porphyrin iron(III) chloride, Fe(TPFP)Cl, is one of the halogen substituted tetraphenylporphyrins (TPP) and have been frequently used as a mono oxygen transfer catalyst because of its high reactivity and its high resistence of the porphyrin ring to oxidative degradation. Fe(TPFP)Cl, which is known as the most electron deficient metalloporphyrin,[5] forms a very stable non-radical oxoferryl porphyrin through the reaction with oxidant such as *m*-chloroperoxybenzoic acid (mCPBA) at low temperature. That is contrast to a electron rich iron tetramesityl porphyrin chloride, Fe(TMP)Cl, which forms the π-cation radical oxoferryl porphyrin upon oxidation.[6] Thus, Fe(TFPF)Cl is an excellent target material to investigate the major role of porphyrin moeity in the active center of oxidation reaction. Goff *et al.*[7] reported that addition of mCPBA to Fe(TPP)F at -78 ℃ produces a fluorooxo iron(IV) porphyrin π-cation radical and binding of basic, "hard" axial ligand such as fluoride ion might stabilize the highly oxidized iron porphyrin species. The anion ligated oxoferryl porphyrins haven't had much attention. Especially, no vibrational data are available.

In this note, we report the RR spectra of oxoferryl iron porphyrin with fluoride ligand, O=Fe(TPFP)F in the presence or absence of hydrogen bonding, for the first time. We also obtained the RR spectra of O=Fe(TPFP)X (X= $OClO_3^-$, mCB^-). Finally, it is discussed the structure of this species and the magnitude of the trans ligand effect for those three anions in the O=Fe(TPFP)X.

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