

# Synthesis of $\sigma$ -(Vinyl)iron(III) Porphyrins and (Dialkylcarbene)iron(II) Porphyrins through the Hydrometallation of Alkynes with Iron(III) Porphyrins and NaBH<sub>4</sub>

Jun-ichiro Setsune,\* Yoshihiro Ishimaru and Akira Sera

Department of Chemistry, Faculty of Science, Kobe University, Nada, Kobe 657, Japan

Treatment of Fe<sup>III</sup>(tpp)Cl (tpp = *meso*-tetraphenylporphyrin dianion) with excess of NaBH<sub>4</sub> and terminal alkynes in toluene-methanol afforded (dialkylcarbene)Fe<sup>II</sup>(tpp), while the reaction with internal alkynes afforded  $\sigma$ -(vinyl)Fe<sup>III</sup>(tpp) in good yields.

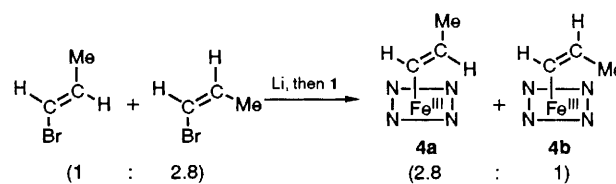
It is known that cytochrome P450 and other haem proteins are alkylated at iron by treatment with organic hydrazines under aerobic conditions and with polyhalogenated compounds under anaerobic conditions.<sup>1</sup> These organometallic reactions of haem proteins are of great significance in the events of metabolic processes. In this paper is disclosed new reactions of iron porphyrins which lead to effective formation of such organoiron porphyrins,  $\sigma$ -(vinyl)iron(III) porphyrins and (dialkylcarbene)iron(II) porphyrins, through the hydrometallation of alkynes in the presence of excess of NaBH<sub>4</sub>.

Fe<sup>III</sup>(tpp)Cl **1** (50 mg) was treated with hex-3-yne (0.6 ml) and NaBH<sub>4</sub> (200 mg) in toluene-methanol (4 ml:0.1 ml) under argon at room temperature. The reaction was complete in a couple of minutes to give a red solution, the UV-VIS spectrum of which was indicative of almost quantitative formation of organoiron porphyrins ( $\lambda_{\text{max}}$ /nm 410, 520 and 549). Chromatographic separation on basic alumina with CH<sub>2</sub>Cl<sub>2</sub> under argon afforded purple powders (91% yield) which showed a molecular ion due to (C<sub>6</sub>H<sub>11</sub>)Fe<sup>III</sup>(tpp) (*m/z* 750) in the mass spectrum and satisfactory elemental analyses. The <sup>1</sup>H NMR spectrum in a degassed C<sub>6</sub>D<sub>6</sub> solution showed signals due to a paramagnetic  $\sigma$ -type organoiron(III) porphyrin (*S* = 1/2) along with a small amount of a diamagnetic iron porphyrin. The signals at  $\delta$  -248, -103 and 169 (23 °C) are assigned to the 4-CH, 2-CH<sub>2</sub> and 5-CH<sub>2</sub> protons, respectively, of  $\sigma$ -(hex-3-en-3-yl)Fe<sup>III</sup>(tpp) **2** on the basis of the isotropic shifts, the major parts of which may be accounted for by the contact shifts due to  $\sigma$ - and  $\pi$ -transmission of the spin density of iron. The use of hex-2-yne in the above procedure afforded a mixture of two isomeric  $\sigma$ -(vinyl)Fe<sup>III</sup>(tpp) derivatives, **3a** and **3b**. The ratio of the hex-2-en-2-yl **3a** and hex-2-en-3-yl **3b** compounds was 1.9:1 on the basis of their <sup>1</sup>H NMR signal intensities (see Table 1).

The <sup>1</sup>H NMR spectrum of **2** was identical with those of the organoiron(III) porphyrins synthesized by treating **1** with organolithium reagents derived from *E*- and *Z*-(hex-3-en-3-yl)iodide. This means that the stereochemical integrity of the (hex-3-en-3-yl)lithium reagents was lost during the reaction with **1**. In fact, treatment of a mixture of *trans*- and

*cis*-1-bromoprop-1-ene (1:2.8 ratio) with lithium and then with **1** in diethyl ether gave a mixture of *trans*- and *cis*- $\sigma$ -(prop-1-en-1-yl)Fe<sup>III</sup>(tpp) isomers **4a** and **4b**, in the ratio of 2.8:1 (ratio coincidentally reversed) based on <sup>1</sup>H NMR analysis (see Scheme 1). The signals at  $\delta$  -214 and -402 of **4a** and **4b**, respectively, are associated with the *cis*- and *trans*- $\beta$ -vinyl protons, respectively, relative to iron, on the basis of the fact that the contact shift in the paramagnetic <sup>1</sup>H NMR spectrum is roughly proportional to the spin-spin coupling constant in the diamagnetic spectrum. Thus, the *Z*-hexenyl structure of **2**, **3a** and **3b** could be determined by comparing the  $\beta$ -vinyl proton chemical shifts ( $\delta$  *ca.* -250) of **2**, **3a** and **3b** with those of **4a** and **4b**.

When **1** was allowed to react with hex-1-yne and pent-1-yne in toluene-methanol (4 ml:1.2 ml) in the presence of NaBH<sub>4</sub>, the diamagnetic iron porphyrins **6** and **7** were formed in 95 and 81% yields, respectively. Their <sup>1</sup>H NMR chemical shifts (Table 1) and UV-VIS absorption maxima ( $\lambda_{\text{max}}$ /nm 410, 520 and 546) are similar to those of (carbene)Fe<sup>II</sup>(tpp) complexes recently reported by Mansuy's group.<sup>2</sup> The mass spectrum of **6** showed a molecular ion due to (C<sub>6</sub>H<sub>12</sub>)Fe<sup>II</sup>(tpp) (*m/z* 751). Peaks due to Fe<sup>II</sup>(tpp) (*m/z* 667: M - 84 and 668: M - 83) and to (C<sub>6</sub>H<sub>12</sub>)<sub>2</sub>Fe<sup>II</sup>(tpp) (*m/z* 835: M + 84) were also observed. This disproportionation in the mass spectrum is frequently noted in carbene complexes of metalloporphyrins.<sup>3</sup> These spectroscopic data of **6** are consistent with a dialkylcarbene complex, (methylbutylcarbene)Fe<sup>II</sup>(tpp). Although a large number of (carbene)Fe<sup>II</sup> porphyrins have been prepared by

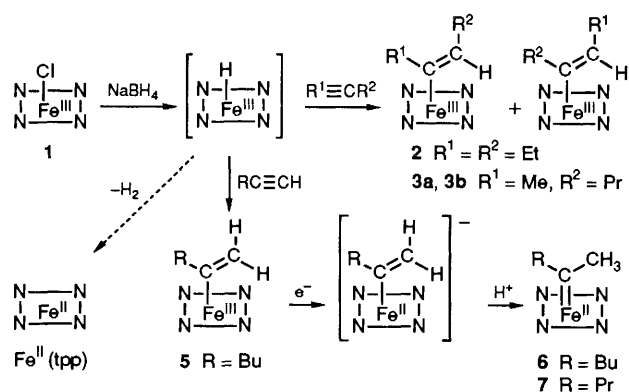


Scheme 1

Table 1 <sup>1</sup>H NMR data of  $\sigma$ -(vinyl)Fe<sup>III</sup>(tpp) and (carbene)Fe<sup>II</sup>(tpp) in C<sub>6</sub>D<sub>6</sub> at 23 °C

Complex	Chemical shift, $\delta$ from Me <sub>4</sub> Si <sup>a</sup>							
	Porphyrin $\beta$ -pyrrole	Axial organo ligand						
		$\gamma'$	$\beta'$	$\alpha$	$\beta$	$\gamma$	$\delta$	$\epsilon$
<b>2</b> (tpp)Fe <sup>III</sup> -C(Et)=CH(Et)	-14.3(8H)	10.9(3H)	-103(2H)	—	-248(1H)	169(2H)	N.d.	—
<b>3a</b> (tpp)Fe <sup>III</sup> -C(Me)=CH(Pr)	-14.3(8H)	—	-89.6(3H)	—	-253(1H)	189(2H)	N.d.	N.d.
<b>3b</b> (tpp)Fe <sup>III</sup> -C(Pr)=CH(Me)	-14.3(8H)	N.d.	-103(2H)	—	-248(1H)	160(3H)	—	—
<b>4a</b> (tpp)Fe <sup>III</sup> -CH=CH(Me) ( <i>trans</i> )	-16.3(8H)	—	—	229(1H)	-214(1H)	160(3H)	—	—
<b>4b</b> (tpp)Fe <sup>III</sup> -CH=CH(Me) ( <i>cis</i> )	-15.5(8H)	—	—	266(1H)	-402(1H)	127(3H)	—	—
<b>5</b> (tpp)Fe <sup>III</sup> -C(Bu)=CH <sub>2</sub>	-16.3(8H)	21.0(2H)	-64.2(2H)	—	-333(1H)	—	—	—
					-192(1H)			
<b>6</b> (tpp)Fe <sup>II</sup> =C(Me)(Bu)	8.68(8H)	—	-2.12(3H)	—	-1.62(2H) <sup>b</sup>	-1.30(2H) <sup>c</sup>	-0.21(2H) <sup>d</sup>	0.11(3H) <sup>b</sup>
<b>7</b> (tpp)Fe <sup>II</sup> =C(Me)(Pr)	8.68(8H)	—	-2.15(3H)	—	-1.72(2H) <sup>b</sup>	-1.17(2H) <sup>d</sup>	-0.21(3H) <sup>b</sup>	—

<sup>a</sup>  $\gamma'$ -,  $\beta'$ -,  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -,  $\epsilon$ - are positions relative to the metal centre. Resonance positions for  $\epsilon'$ - (for **5**) and  $\delta'$ -protons (for **5** and **3b**) could not be determined because of overlap with aromatic protons or signals due to diamagnetic impurities. Signal multiplicity is singlet unless otherwise noted. <sup>b</sup> Triplet. <sup>c</sup> Quintet. <sup>d</sup> Sextet.



Scheme 2

Mansuy and coworkers from polyhalogenated compounds or diazo compounds, **6** and **7** are the first examples of dialkylcarbene complexes of Fe<sup>II</sup> porphyrins.

When **1** was allowed to react with hex-1-yne and NaBH<sub>4</sub> in toluene-THF (4 ml : 3 ml) or in toluene-methanol (4 ml : 0.1 ml), a considerable amount of the  $\sigma$ -(vinyl)Fe<sup>III</sup> complex **5** was formed along with **6**. This suggests that terminal alkynes undergo regioselective hydrometallation to give a  $\sigma$ -(alk-1-en-2-yl)Fe<sup>III</sup> complex which is subsequently reduced and protonated under the reaction conditions as shown in Scheme 2. In accord with this mechanism, approximately one-third of the  $\beta$ -methyl protons of **6** was deuteriated (<sup>2</sup>H content 40% by <sup>1</sup>H NMR) when NaBD<sub>4</sub>, hex-1-yne, C<sub>7</sub>H<sub>8</sub> and CH<sub>3</sub>OH were employed, whereas two-thirds of the  $\beta$ -methyl protons of **6** were deuteriated (<sup>2</sup>H content 70%) when NaBD<sub>4</sub>, hex-1-yne, C<sub>7</sub>H<sub>8</sub> and CD<sub>3</sub>OD were employed. NaBH<sub>4</sub> dissolves only partially in the present solvent system (toluene-methanol) and an increase in the proportion of methanol increases the concentration of NaBH<sub>4</sub> in the solvent and thus facilitates the reduction of **5**. Furthermore, the protonation of an anionic intermediate would be favoured in a methanol-rich solvent. The intermediacy of the anionic  $\sigma$ -(vinyl)Fe<sup>II</sup>(tpp) in the conversion of **5** to **6** seems reasonable, since it has been shown that such anionic  $\sigma$ -(vinyl)Fe<sup>II</sup> porphyrins are formed *via* electrochemical reduction (-0.6 V vs. standard calomel electrode) of  $\sigma$ -(vinyl)Fe<sup>III</sup> porphyrins.<sup>2a,4</sup> The present reaction is closely related to the reaction of Fe<sup>II</sup> porphyrins with polyhalogenated compounds in the presence of a reducing agent which gives (carbene)Fe<sup>II</sup> porphyrins *via* elimination of halide anion from anionic  $\sigma$ -( $\alpha$ -halogenoalkyl)Fe<sup>II</sup> porphyrin intermediates.<sup>5</sup>

$\sigma$ -Type organoiron(III) porphyrins have so far been prepared by the reaction of Fe<sup>III</sup>, Fe<sup>II</sup> and Fe<sup>I</sup> porphyrins with, for

example, Grignard reagents,<sup>6a</sup> organic hydrazines<sup>6b</sup> and alkyl halides,<sup>6c</sup> respectively. The present reaction is the first example of hydrometallation of unsaturated compounds with an iron porphyrin. As in our recent report on a cobalt porphyrin,<sup>7</sup> a hydridometal porphyrin intermediate is likely to be responsible for this hydrometallation. Although **1** is reduced to Fe<sup>II</sup>(tpp) immediately by NaBH<sub>4</sub>, H-Fe<sup>III</sup>(tpp) would be formed initially and such a hydridometal porphyrin would undergo bimolecular H<sub>2</sub> elimination as shown with rhodium and ruthenium.<sup>8</sup> While we have found that alkenes are hydrometallated with **1** to give a mixture of  $\sigma$ -(alkyl)-Fe<sup>III</sup>(tpp) and Fe<sup>II</sup>(tpp) under the same reaction conditions as noted above,<sup>9</sup> **2**, **3a** and **3b** were not accompanied by Fe<sup>II</sup>(tpp). This suggests that alkyne hydrometallation is much faster than the bimolecular H<sub>2</sub> elimination of H-Fe<sup>III</sup>(tpp) (see Scheme 2).

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## References

- H. H. Ruf, H. Ahr, W. Nastainczyk, V. Ullrich, D. Mansuy, J.-P. Battioni, R. Montiel-Montoya and A. Trautwein, *Biochemistry*, 1984, **23**, 5300; K. L. Kunze and P. R. Ortiz de Montellano, *J. Am. Chem. Soc.*, 1983, **105**, 1380.
- (a) I. Artaud, N. Gregoire, P. Leduc and D. Mansuy, *J. Am. Chem. Soc.*, 1990, **112**, 6899; (b) I. Artaud, N. Gregoire, J.-P. Battioni, D. Dupre and D. Mansuy, *J. Am. Chem. Soc.*, 1988, **110**, 8714.
- J.-i. Setsune and D. Dolphin, *Organometallics*, 1984, **3**, 440; A. W. Johnson, D. Ward, P. Batten, A. L. Hamilton, G. Schelton and C. M. Elson, *J. Chem. Soc., Perkin. Trans. 1*, 1975, 2076.
- J.-P. Battioni, D. Lexa, D. Mansuy and J.-M. Saveant, *J. Am. Chem. Soc.*, 1983, **105**, 207; D. Lexa and J.-M. Saveant, *J. Am. Chem. Soc.*, 1982, **104**, 3503.
- D. Mansuy and J.-P. Battioni, *J. Chem. Soc., Chem. Commun.*, 1982, 638.
- (a) P. Cocolios, G. Lagrange and R. Guilard, *J. Organomet. Chem.*, 1983, **253**, 65; (b) J.-P. Battioni, J. P. Mahy, G. Gillet and D. Mansuy, *J. Am. Chem. Soc.*, 1983, **105**, 1399; (c) D. Lexa, J. Mispelter and J.-M. Saveant, *J. Am. Chem. Soc.*, 1981, **103**, 6806.
- J.-i. Setsune, Y. Ishimaru, T. Moriyama and T. Kitao, *J. Chem. Soc., Chem. Commun.*, 1991, 555.
- J.-i. Setsune, Z.-I. Yoshida and H. Ogoshi, *J. Chem. Soc., Perkin. Trans. 1*, 1982, 983; J. P. Collman, J. E. Hutchison, P. S. Wagenknecht, N. S. Lewis, M. A. Lopez and R. Guilard, *J. Am. Chem. Soc.*, 1990, **112**, 8206.
- J.-i. Setsune, Y. Ishimaru and A. Sera, unpublished result.