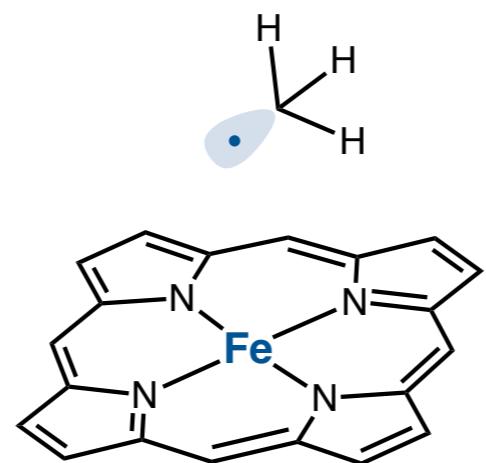


*Metal-alkyl complexes of iron and cobalt porphyrins:  
photonic and non-photonic chemistry*



Marissa Lavagnino

MacMillan Group Meeting

30 September 2020

# *Iron and cobalt: a pair of mid-row metals*

**earlier than nickel and copper**

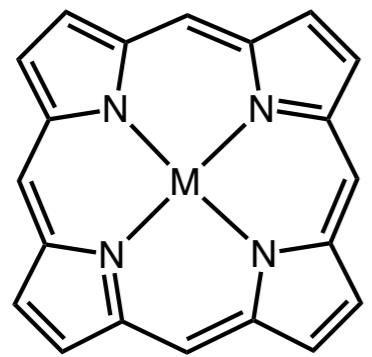
**lighter than rhodium and ruthenium**

## **earth-abundant and biologically relevant**

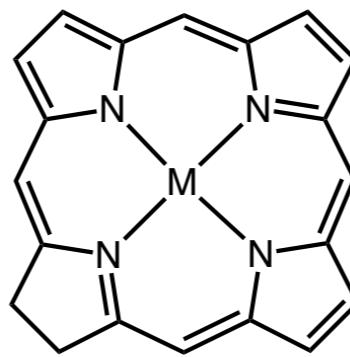
1 IA	lighter than rhodium and ruthenium																		18 VIIA																	
1 IA	earth-abundant and biologically relevant																		18 VIIA																	
1 H Hydrogen 1.008	2 IIA	3 Li Lithium 6.94	4 Be Beryllium 9.0121831	5 VB	6 VIB	7 VIIIB	d <sup>8</sup>	d <sup>9</sup>	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	2 He Helium 4.002602																	
3 Na Sodium 22.98976928	12 Mg Magnesium 24.305	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIIB	Fe	Co	Mn	Cr	V	Ti	Sc	Ca	K Potassium 39.0983	Al	Si	P Phosphorus 30.973761998	Cl Chlorine 35.45	Ne Neon 20.1797																
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955908	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938044	26 Fe Iron 55.845	27 Co Cobalt 58.933194	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.630	33 As Arsenic 74.921595	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798	37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90584	40 Zr Zirconium 91.224	41 Nb Niobium 92.90637	42 Mo Molybdenum 95.95	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.293	
55 Cs Caesium 132.90545196	56 Ba Barium 137.327	57 - 71 Lanthanoids		72 Hf Hafnium 178.49	73 Ta Tantalum 180.94788	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 186.207	77 Ir Iridium 192.217	78 Pt Platinum 195.084	79 Au Gold 196.966569	80 Hg Mercury 200.592	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.98040	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)	87 Fr Francium (223)	88 Ra Radium (226)	89 - 103 Actinoids	104 Rf Rutherfordium (267)	105 Db Dubnium (268)	106 Sg Seaborgium (269)	107 Bh Bohrium (270)	108 Hs Hassium (269)	109 Mt Meitnerium (278)	110 Ds Darmstadtium (281)	111 Rg Roentgenium (282)	112 Cn Copernicium (285)	113 Nh Nihonium (286)	114 Fl Flerovium (289)	115 Mc Moscovium (289)	116 Lv Livermorium (293)	117 Ts Tennessine (294)	118 Og Oganesson (294)

57 <b>La</b> Lanthanum 138.90547	58 <b>Ce</b> Cerium 140.116	59 <b>Pr</b> Praseodymium 140.90766	60 <b>Nd</b> Neodymium 144.242	61 <b>Pm</b> Promethium (145)	62 <b>Sm</b> Samarium 150.36	63 <b>Eu</b> Europium 151.964	64 <b>Gd</b> Gadolinium 157.25	65 <b>Tb</b> Terbium 158.92535	66 <b>Dy</b> Dysprosium 162.500	67 <b>Ho</b> Holmium 164.93033	68 <b>Er</b> Erbium 167.259	69 <b>Tm</b> Thulium 168.93422	70 <b>Yb</b> Ytterbium 173.045	71 <b>Lu</b> Lutetium 174.9668
89 <b>Ac</b> Actinium (227)	90 <b>Th</b> Thorium 232.0377	91 <b>Pa</b> Protactinium 231.03588	92 <b>U</b> Uranium 238.02891	93 <b>Np</b> Neptunium (237)	94 <b>Pu</b> Plutonium (244)	95 <b>Am</b> Americium (243)	96 <b>Cm</b> Curium (247)	97 <b>Bk</b> Berkelium (247)	98 <b>Cf</b> Californium (251)	99 <b>Es</b> Einsteinium (252)	100 <b>Fm</b> Fermium (257)	101 <b>Md</b> Mendelevium (258)	102 <b>No</b> Nobelium (259)	103 <b>Lr</b> Lawrencium (266)

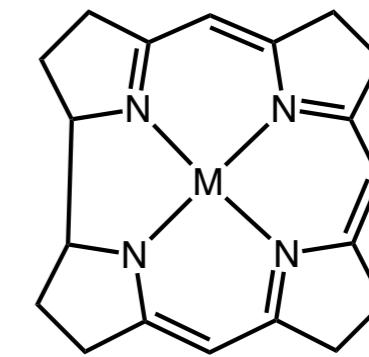
*Nature uses macrocyclic ligands to harness potential of light metals*



Porphyrin (hemes, Fe)



Chlorin (chlorophyll, Mg)



Corrin (Vitamin B<sub>12</sub>, Co)

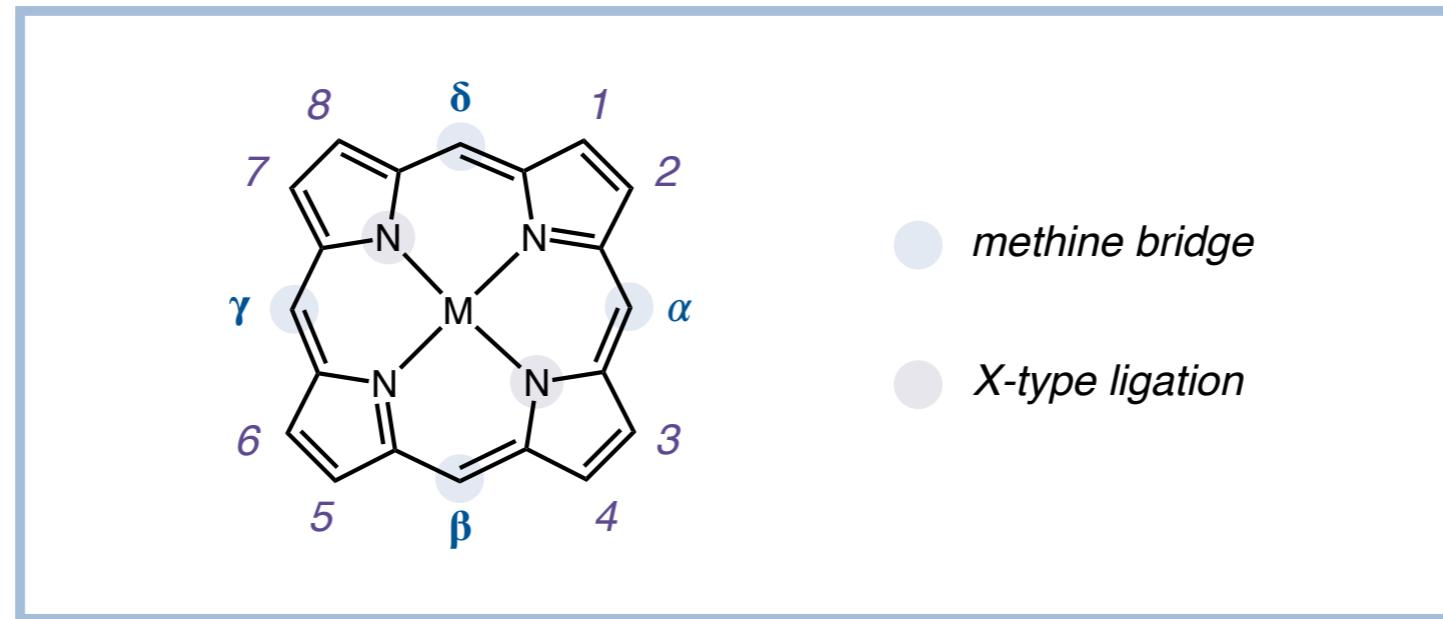
**small changes in *degree of saturation* and *ring size* yield biologically-relevant ligand scaffolds**

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**used by nature to modify reactivity of *abundant* light metals**

## *The porphyrin ligand*

**macrocyclic, tetradentate, dianionic ligand composed of 4 pyrrole rings linked by methine bridges**



**Common nomenclature shortens ligand name to an acronym of substituents:**

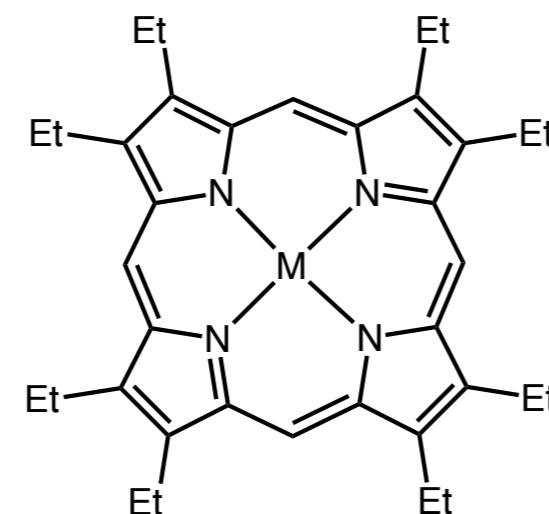
**M(OEP)**

number of substituents “octa”

type of substituent “ethyl”

## *The porphyrin ligand*

**macrocyclic, tetradentate, dianionic ligand composed of 4 pyrrole rings linked by methine bridges**



**M(OEP)**

*octaethylporphyrin*

Common nomenclature shortens ligand name to an acronym of substituents:

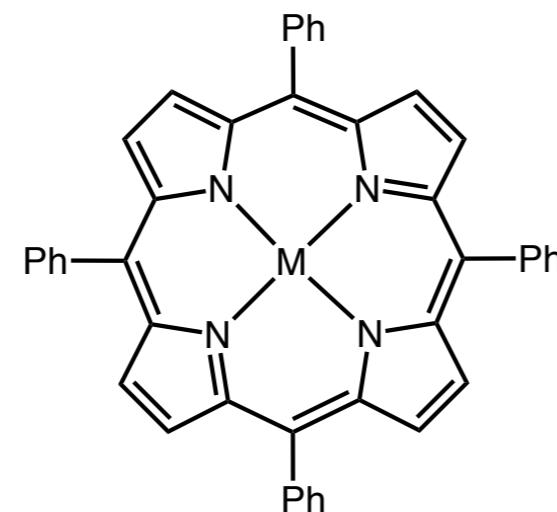
**M(OEP)**

number of substituents “octa”

type of substituent “ethyl”

## *The porphyrin ligand*

**macrocyclic, tetradentate, dianionic ligand composed of 4 pyrrole rings linked by methine bridges**



**M TPP**

*tetraphenylporphyrin*

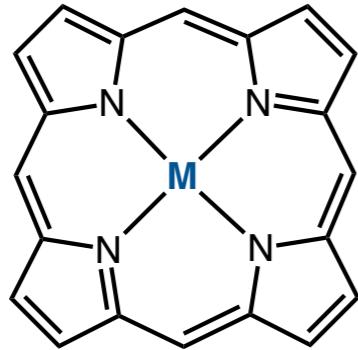
Common nomenclature shortens ligand name to an acronym of substituents:

**M(OEP)**

number of substituents “octa”

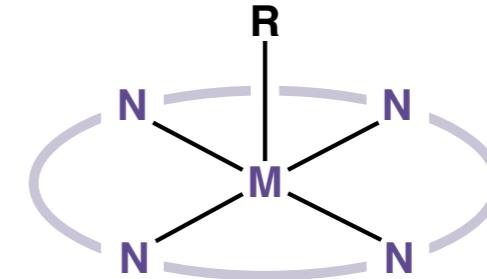
type of substituent “ethyl”

## *The complexes of interest for today's talk*



### Fe and Co porphyrin complexes

characterization, reactivity, etc.



### Fe- and Co-alkyl porphyrin complexes

(porphyrin ring abbreviated for clarity)

***How do these complexes behave under photonic and non-photonic conditions?***

# *Outline*

## ***Characterization of metal porphyrin (alkyl) complexes***

I. molecular and electronic structure

II. metal-carbon bond strengths

III. electrochemical data

IV. synthesis and stability

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## ***Reactivity of metal porphyrin (alkyl) complexes***

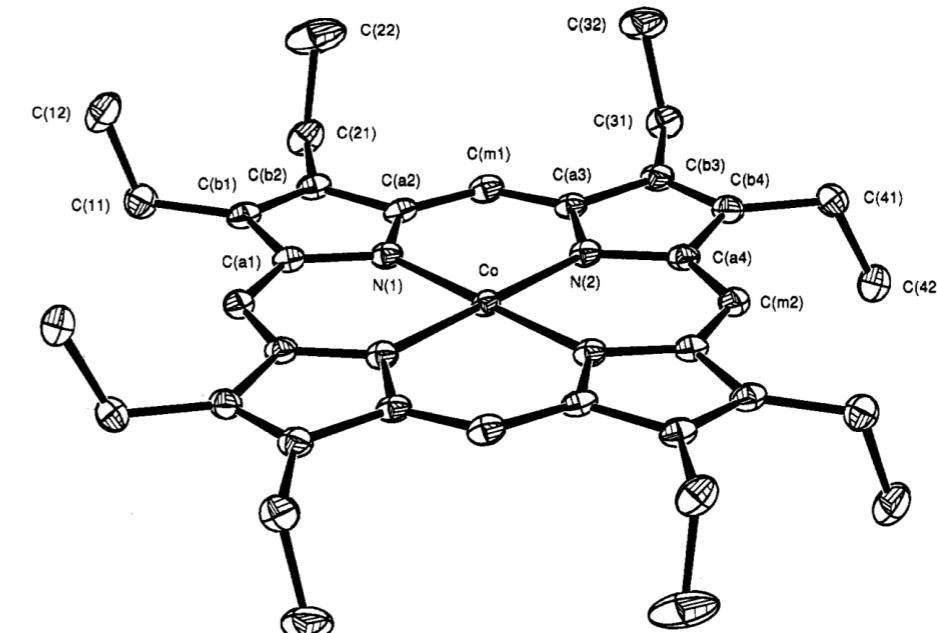
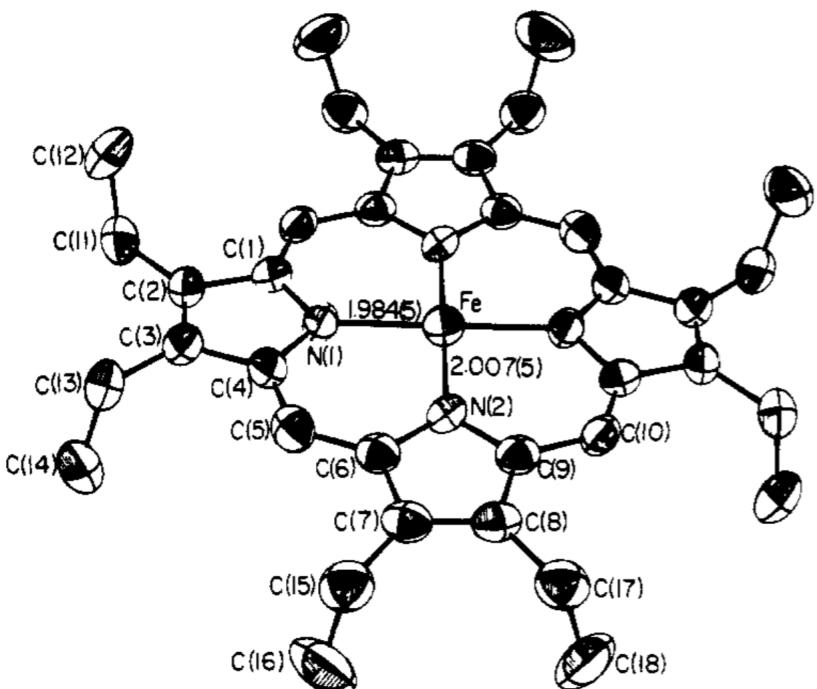
I. photolysis of metal-ligand bonds in porphyrin complexes (*precatalyst activation*)

A. photochemistry of metal porphyrins

II. alkylation of iron porphyrins by nucleophilic displacement (*substrate activation*)

III. the S<sub>H</sub>2 mechanism and metal porphyrins (*bond formation*)

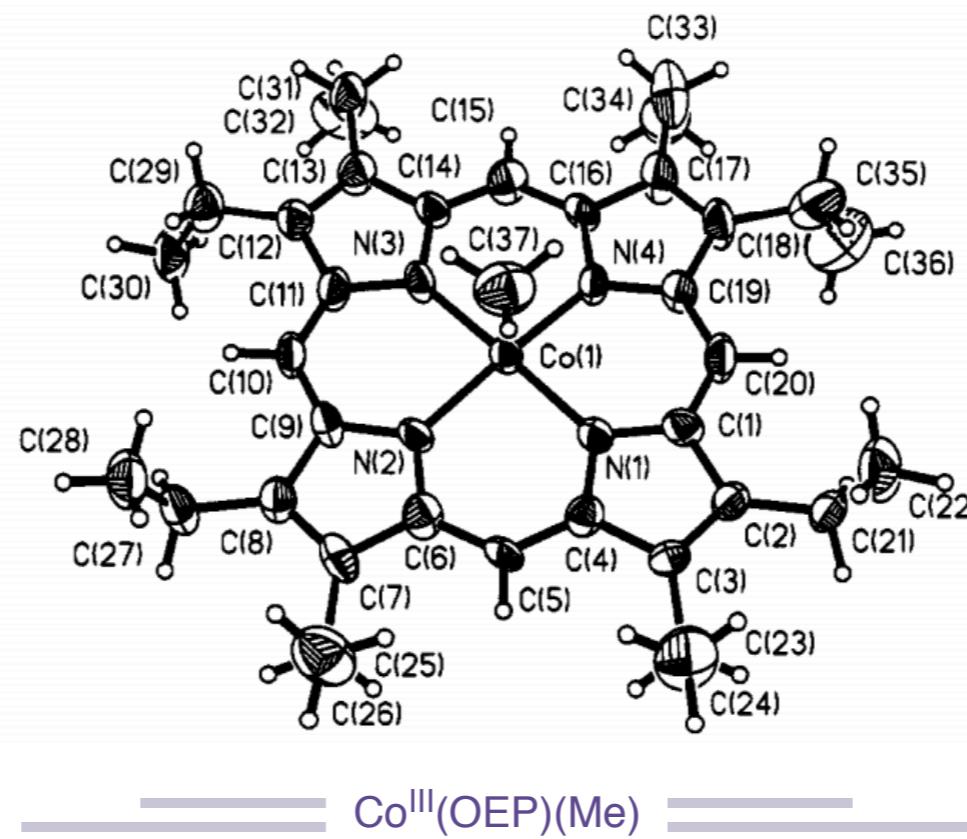
# *Crystal structures of octaethylporphyrin (OEP) complexes*



both complexes are **almost perfectly planar** across the porphyrin plane

(approximate  $D_{4h}$  symmetry)

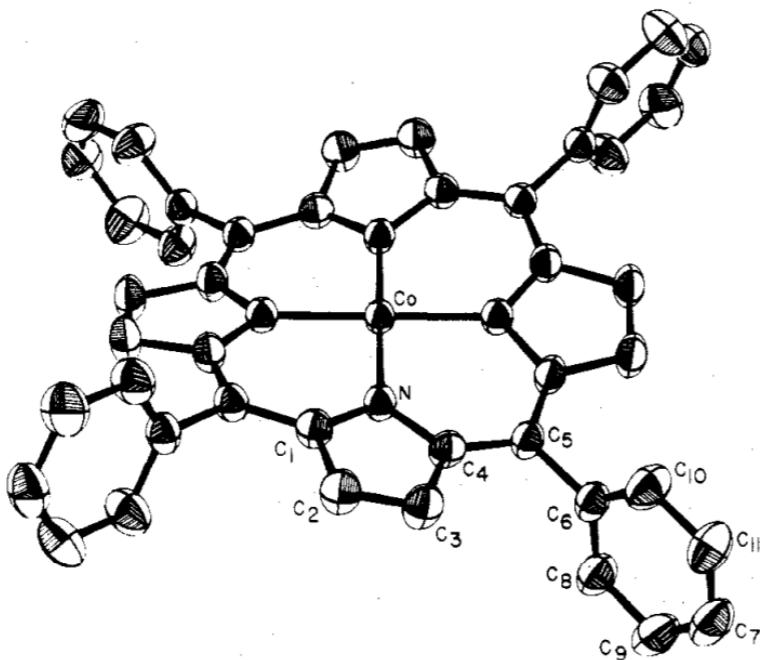
*Alkylation of metal porphyrin results in square pyramidal complex*



Co–C bond: 1.973 Å, Co–N<sub>p</sub> bond: 1.966 Å

5-coordinate square pyramidal complex, symmetry lowered to  $C_{4v}$

# *Crystal structure of tetraphenylporphyrin (TPP) complex*



ruffled complex has  $S_4$  symmetry

Co–N<sub>p</sub> bonds: 1.949(3) Å and 1.951(1) Å

Fe–N<sub>p</sub> bond: 1.972(4) Å

— — — **Co<sup>II</sup>(TPP)** (Fe similar) — — —

geometry determined primarily **by porphyrin substitution**, not identity of metal

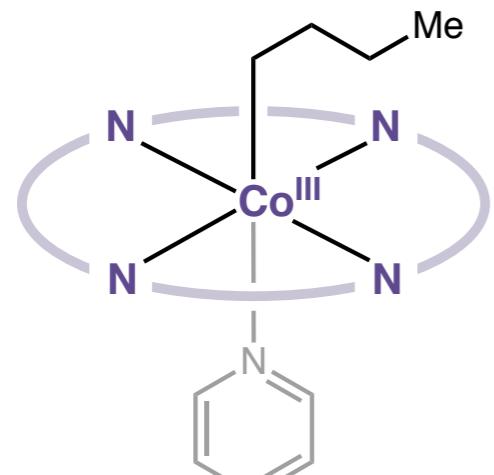
structures are similar **across first row series (Fe, Co, Ni, Cu)**

Collman, J. P.; Hoard, J. L.; Kim, N.; Lang, G.; Reed, C. A. *J. Am. Chem. Soc.* **1975**, 97, 2676.

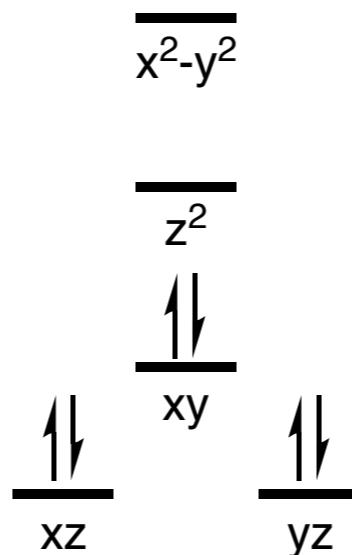
Madura, P.; Scheidt, W. R. *Inorg. Chem.* **1976**, 15, 3182.

# *Electronic configuration of metal porphyrin alkyl complexes*

## — Co<sup>III</sup>(porphyrin)(alkyl) —

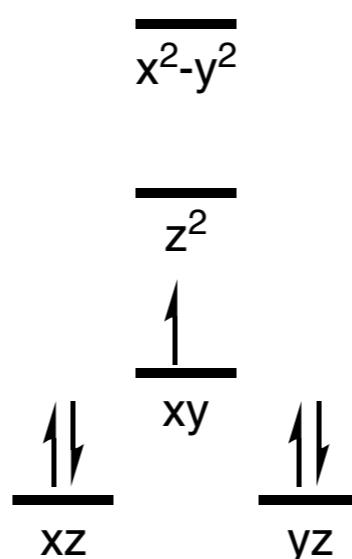
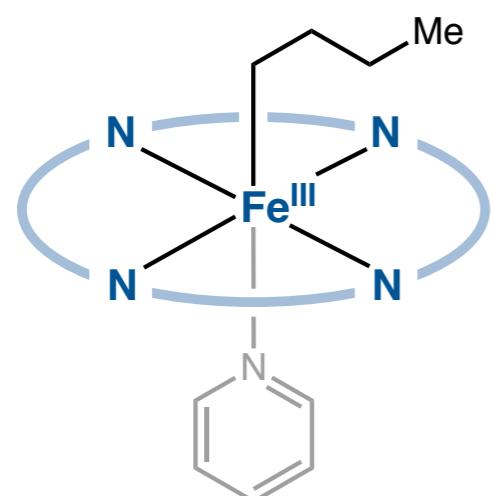


possible apical coordination



diamagnetic complex  
(S = 0)

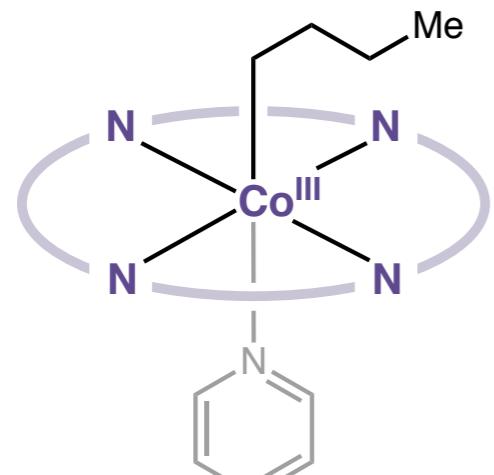
## — Fe<sup>III</sup>(porphyrin)(alkyl) —



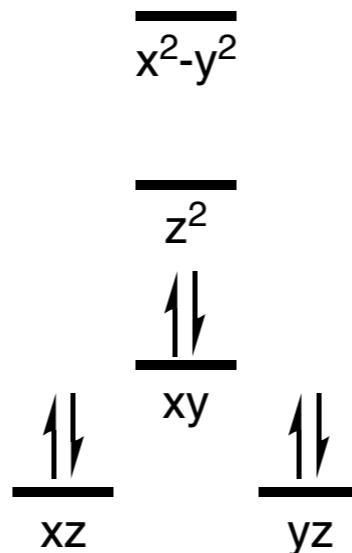
paramagnetic complex  
low spin (S = 1/2)

# *Electronic configuration of metal porphyrin alkyl complexes*

## — Co<sup>III</sup>(porphyrin)(alkyl) —

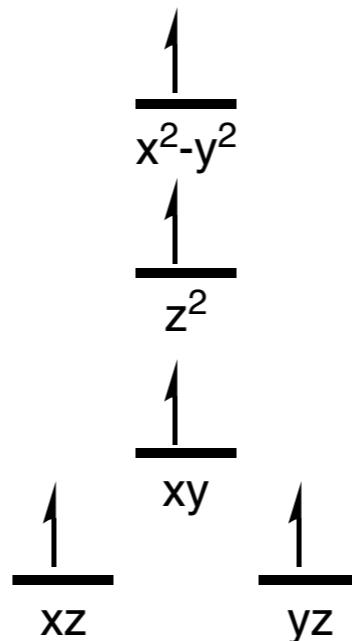
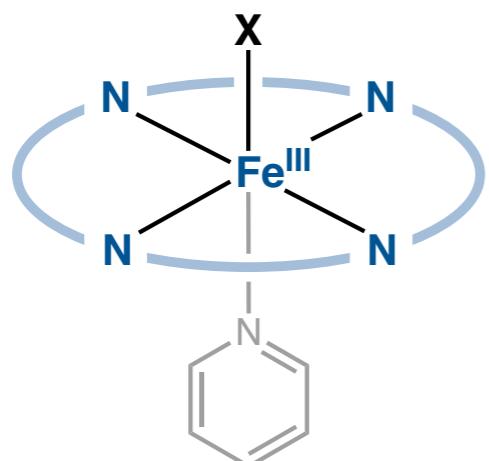


possible apical coordination



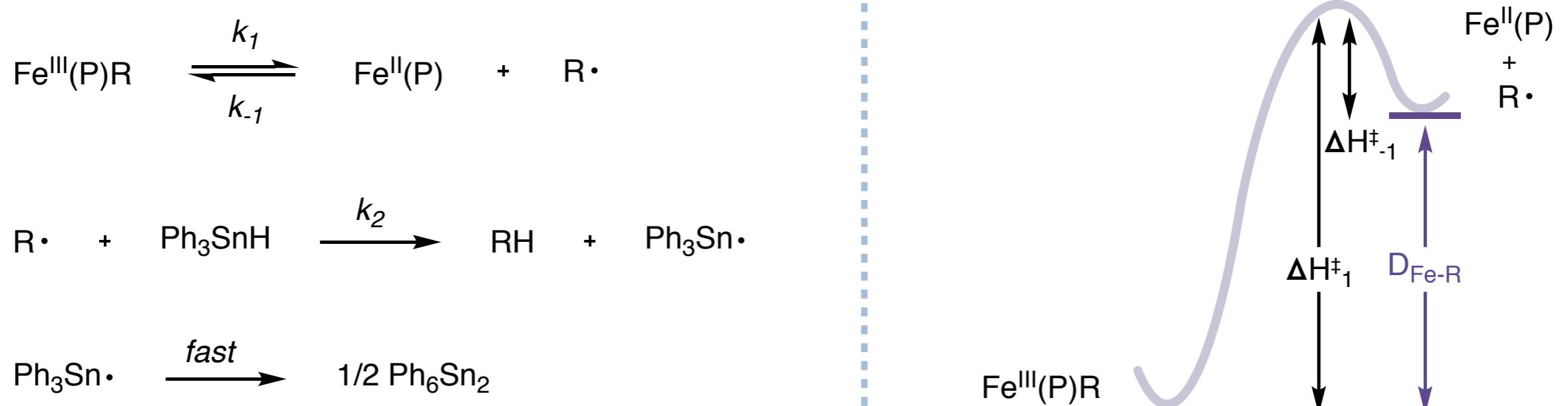
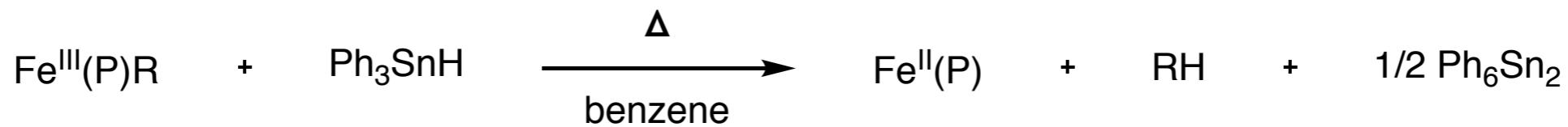
diamagnetic complex  
( $S = 0$ )

## — Fe<sup>III</sup>(porphyrin)(halide) —



paramagnetic complex  
high spin ( $S = 5/2$ )

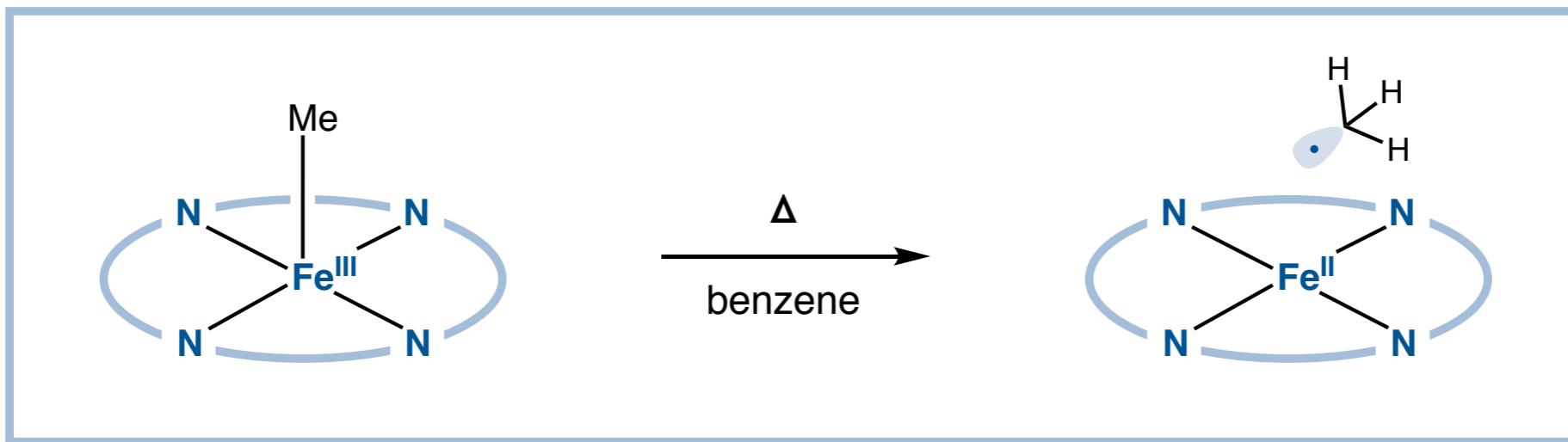
## Measuring Fe–C bond dissociation energies



Assuming 1. excess  $\text{Ph}_3\text{SnH}$  and 2. recombination is diffusion limited ( $\Delta H^\ddagger_{-1} = \Delta H^\ddagger_{\text{viscosity}}$ )

$$D_{\text{Fe-R}} = \Delta H^\ddagger_1 - \Delta H^\ddagger_{\text{viscosity}} = \Delta H^\ddagger_1 - 2 \text{ kcal/mol}$$

# How strong are the Fe–C bonds in an iron porphyrin alkyl complex?



**Table I**

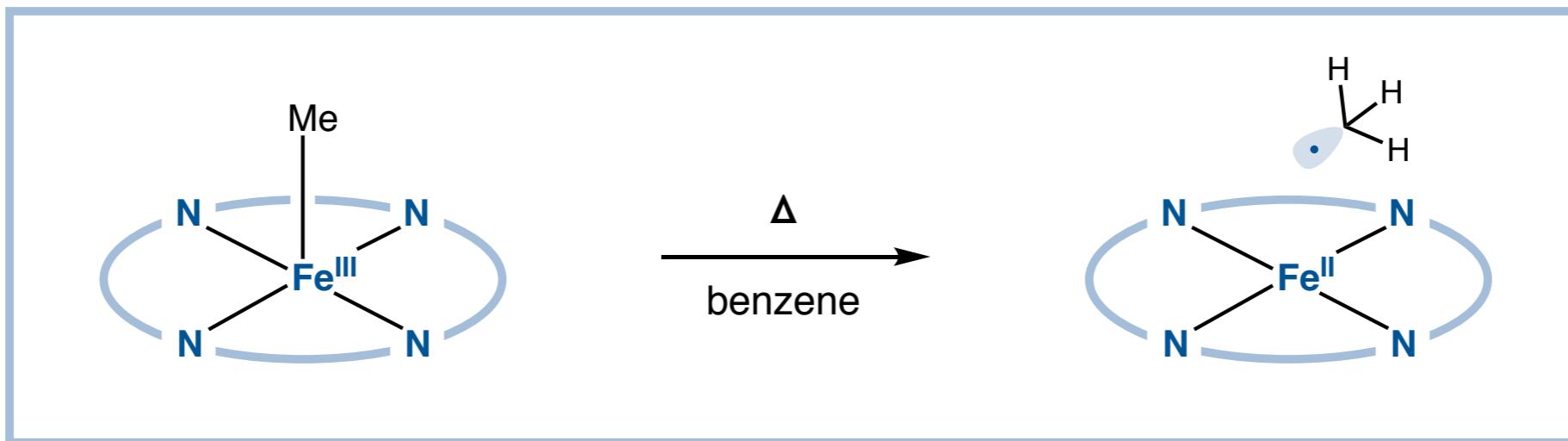
Rate constants, activation parameters and bond dissociation energies for Fe(OEP)R complexes

R	$k_1$ (s⁻¹, 25°C)	$k_{-1}/k_2$ (T, °C) <sup>a</sup>	$k_{-1}$ (M⁻¹ s⁻¹)	$\Delta H^\ddagger$ (kcal mol⁻¹)	$\Delta S^\ddagger$ (cal (mol K)⁻¹)	$D_{\text{Fe}-\text{R}}$ (kcal mol⁻¹)
CH <sub>3</sub>	$2.5 \times 10^{-5}$	155 (70)	$1.4 \times 10^9$	$23.3 \pm 0.4$	$-1.1 \pm 1.2$	21
C <sub>2</sub> H <sub>5</sub>	$1.0 \times 10^{-3}$	117 (60)	$1.0 \times 10^9$	$18.6 \pm 0.6$	$-9.3 \pm 1.7$	17
CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>3</sub>	$3.8 \times 10^{-2}$	998 (15)		$17.3 \pm 1.4$	$-6.6 \pm 4.8$	15
C <sub>6</sub> H <sub>5</sub>	$3.8 \times 10^{-11}$			$33.0 \pm 1.2$	$4.5 \pm 2.9$	31

<sup>a</sup>Temperature at which the ratio  $k_{-1}/k_2$  was measured.

Bond dissociation energy strongly influenced by *proximal* steric environment

## Temperature dependence of homolysis rates for Fe(OEP)(R)



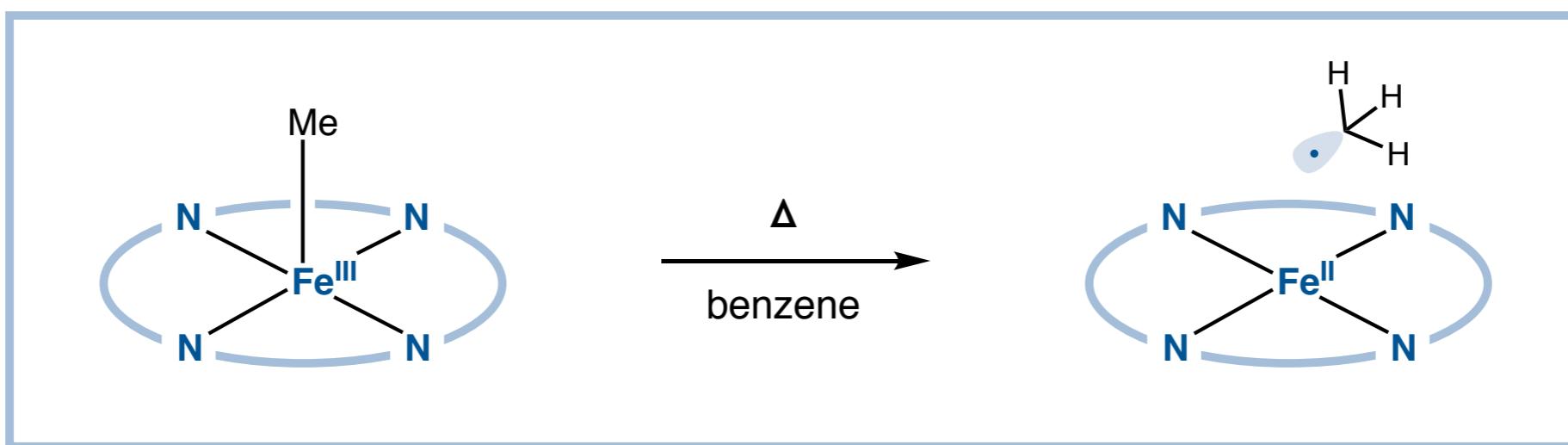
**Table 2**

Temperature dependence of  $k_{\text{obs}}$  for thermolysis of Fe(OEP)R in the presence of limiting concentration of Ph<sub>3</sub>SnH

R	T (°C)	$10^3 k_1 (\text{s}^{-1})$
CH <sub>3</sub>	50	0.62
	55	1.0
	60	1.8
	60	1.8
	65	3.3
	70	5.1
	70	5.2
	70	5.4
	75	8.7

R	T (°C)	$10^3 k_1 (\text{s}^{-1})$
C <sub>2</sub> H <sub>5</sub>	40	0.50
	45	0.86
	50	1.2
	50	1.3
	55	2.1
	60	3.4
	65	4.9

## Temperature dependence of homolysis rates for Fe(OEP)(R)



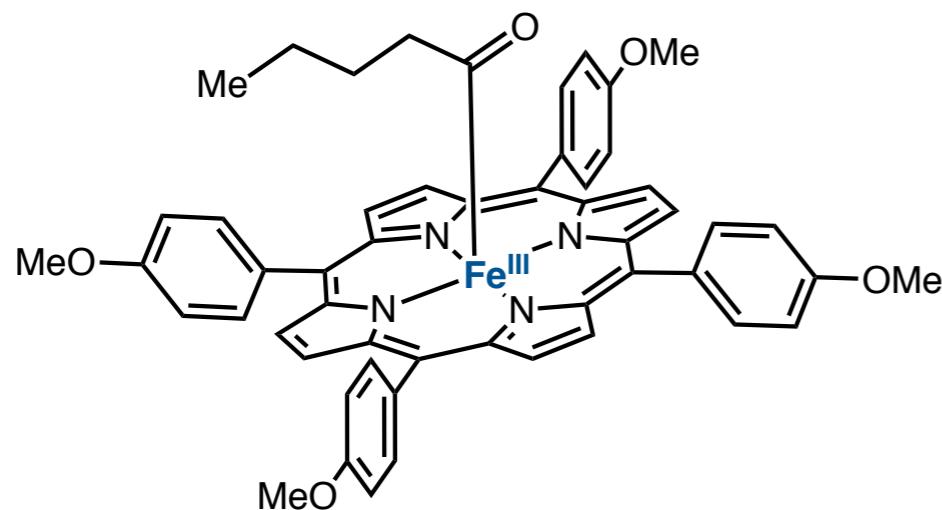
**Table 2**

Temperature dependence of  $k_{\text{obs}}$  for thermolysis of Fe(OEP)R in the presence of limiting concentration of Ph<sub>3</sub>SnH

R	T (°C)	$10^3 k_1 (\text{s}^{-1})$
$(\text{CH}_3)_3\text{CCH}_2$	10	7.2
	15	13
	15	13
	20	21
	20	23
	25	48
	25	50
	30	52
	30	57

R	T (°C)	$10^3 k_1 (\text{s}^{-1})$
$\text{C}_6\text{H}_5$	118.5	0.03
	118.5	0.04
	137	0.24
	141	0.31
	141	0.35
	145	0.52
	150	0.81

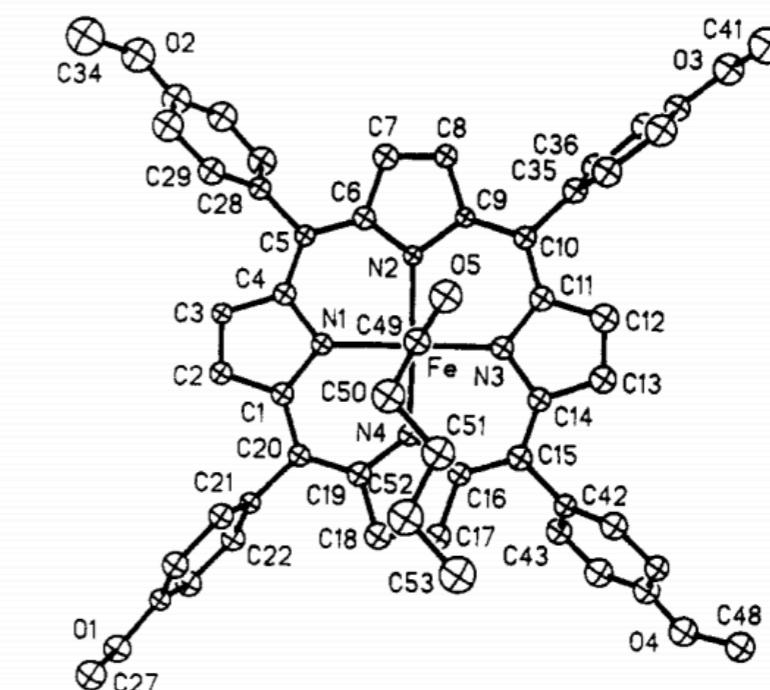
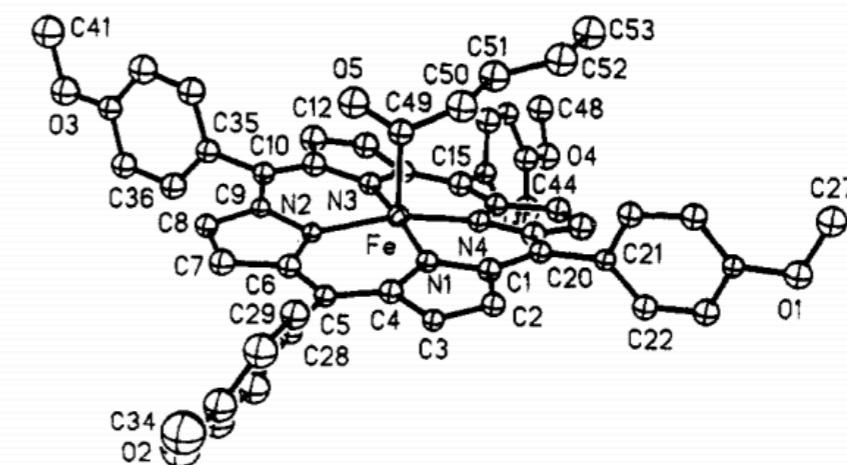
## *The acyl-substituted iron porphyrin*



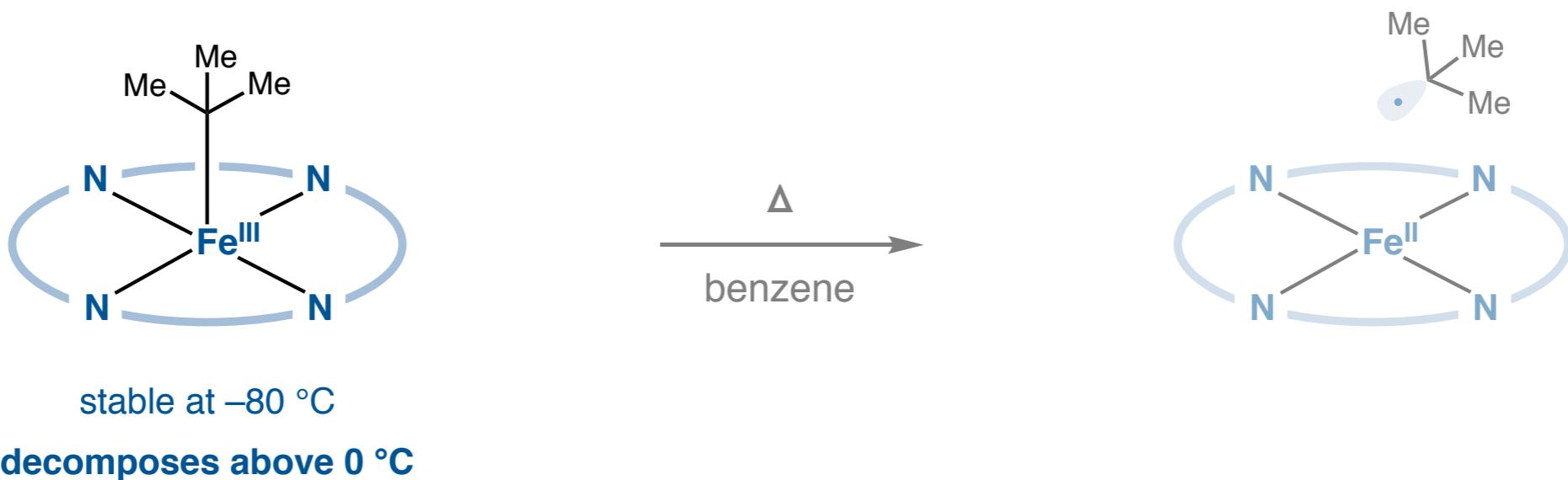
**Fe<sup>III</sup>(TAP)(COC<sub>4</sub>H<sub>9</sub>)**

**stable to visible light**

*"exposure of a toluene solution...to white light from  
a standard slide projector lamp for 7 h  
did not result in significant loss of the complex..."*



## *The question of tert-butyl stability on iron porphyrins*



*“Extensive attempts to prepare  $(\text{TTP})\text{Fe}^{\text{III}}\text{C}(\text{CH}_3)_3$  from...the Grignard reagent*

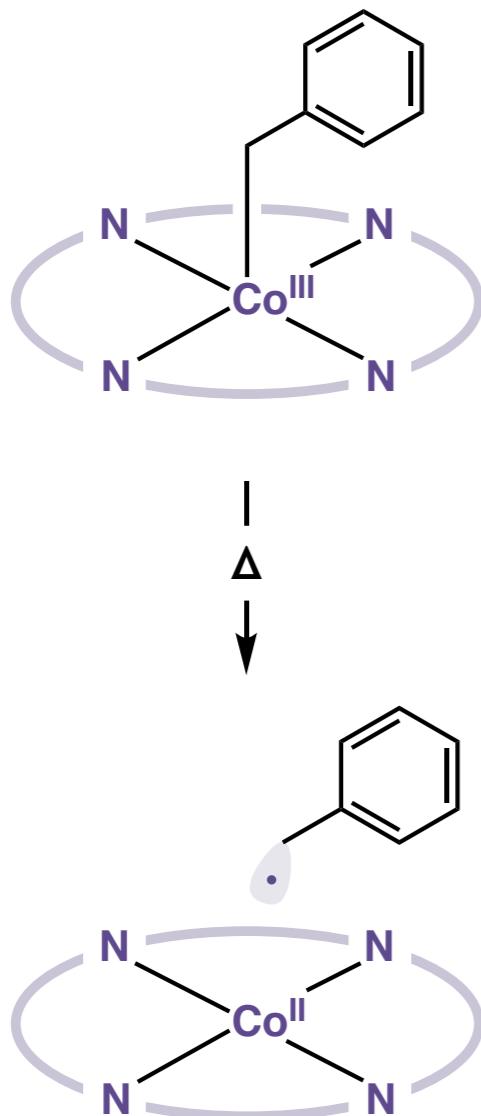
*did not yield...the desired iron-(III)-tert-butyl complex.”*

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*“The major product was  $(\text{TTP})\text{Fe}^{\text{II}}$ , which may have arisen from decomposition of the iron(III)-tert-butyl complex”*

## Comparison to homolysis of Co–C bonds in porphyrin complexes

Co–C BDE's tend to be 10-15 kcal/mol *higher* than Fe–C BDE's for similar complexes



*what is the role  
of added ligand?*

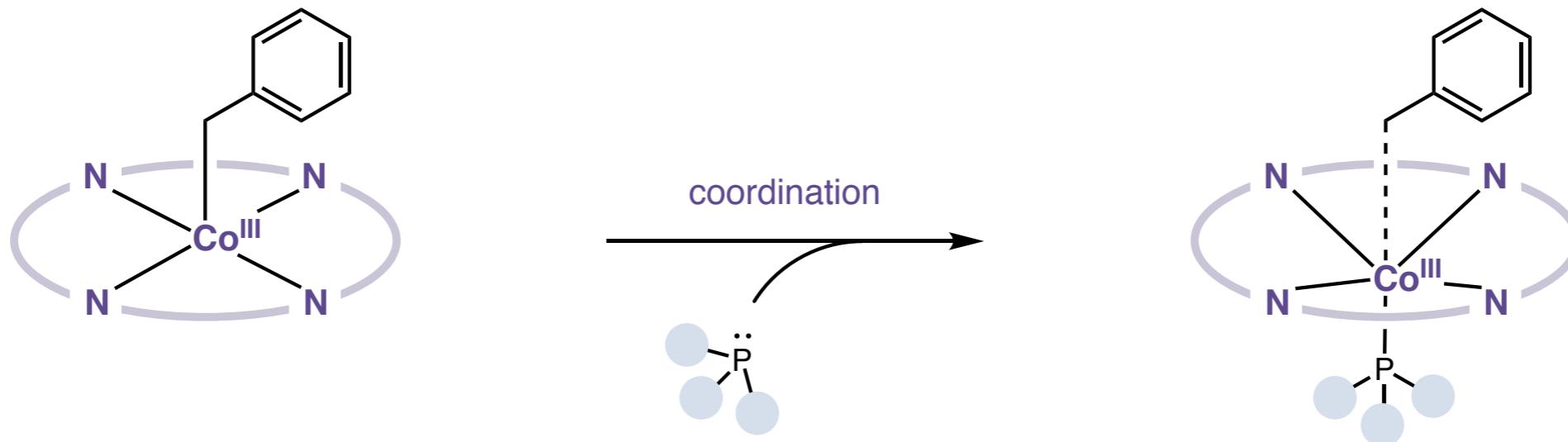
**Table I.** Summary of Kinetic Data

chelate	$PR_3$	$T, ^\circ C$	$10^4 k_1, s^{-1}$	$\Delta H_1^\ddagger, kcal/mol$	$\Delta S_1^\ddagger, cal/(mol K)$	$D_{Co-R}, kcal/mol$
OEP	$PMMe_2Ph$	55.0	0.096	29.1	7	27.1
		65.0	0.31			
		71.5	0.60			
		89.0	6.6			
		90.4	7.7			
$P-n-Bu_3$	$P-n-Bu_3$	65.0	0.031	31.3	7	29.3
		75.0	0.088			
		85.0	0.40			
		90.4	0.80			
		100	2.4			
$PEtPh_2$	$PEtPh_2$	55.0	0.20	28.1	6	26.1
		72.8	2.0			
		85.0	8.2			
		90.4	15			
		50.4	0.46	25.8	2	23.8
$P(c-C_6H_11)_3$	$P(c-C_6H_11)_3$	55.4	0.92			
		60.4	1.6			
		70.4	5.2			
		72.8	0.018	31.6	6	29.6
		82.8	0.069			
		85.0	0.088			
		91.2	0.194			

Geno, M. K.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 1238.

Riordan, C. G.; Halpern, J. *Inorg. Chim. Acta* **1996**, *243*, 19.

## *Bond homolysis promoted by the coordination of a sixth ligand*



**coordination of a strongly donating and/or bulky apical ligand weakens Co–C bond**  
(*trend also shown in the case of Fe*)

**hypothesized to either result from:**

*trans* effect of coordinating ligand

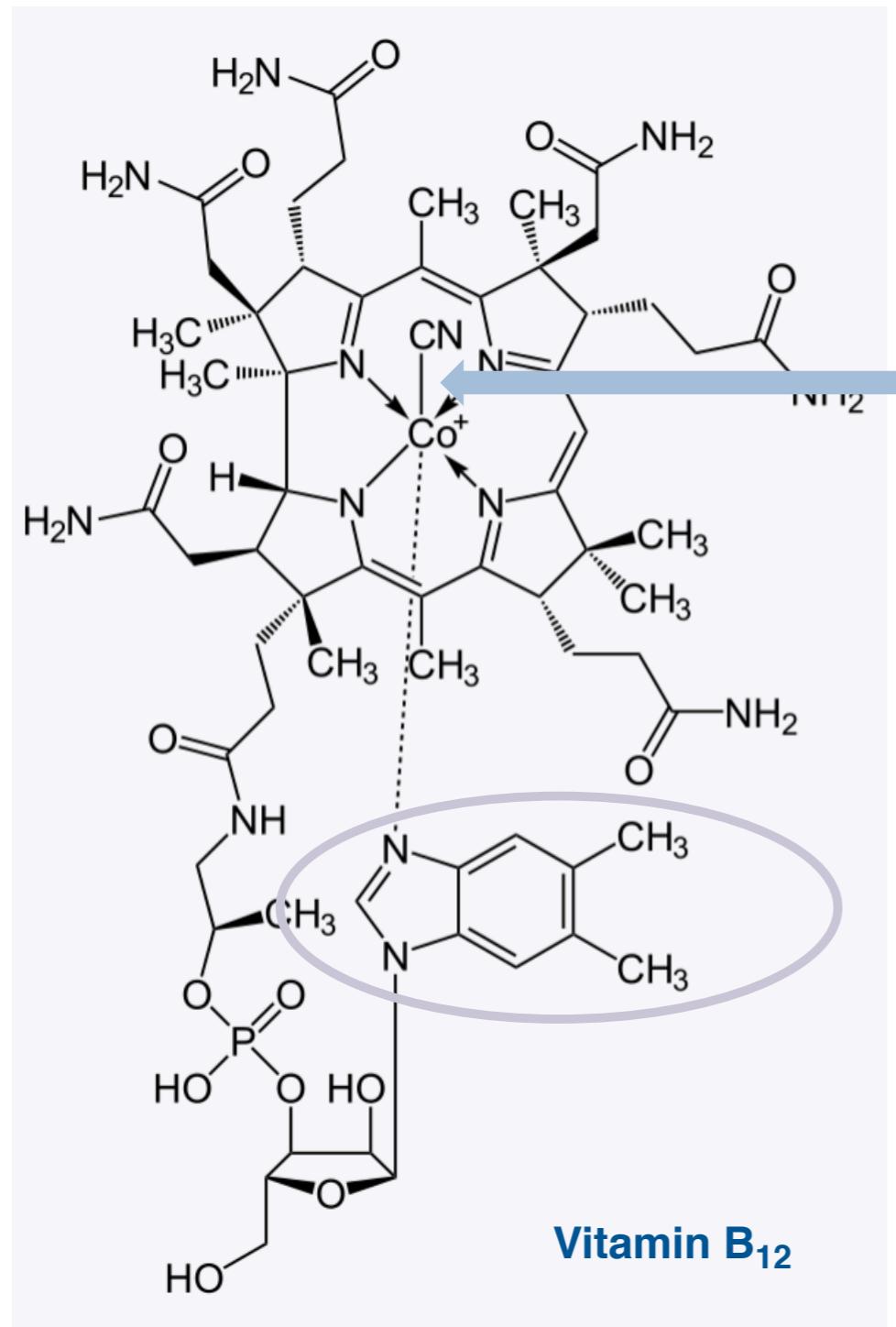
**— OR —**

steric interactions with macrocycle

Geno, M. K.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 1238.

For crystallographic data on effect of pyridine coordination on geometry of  $\text{Co(OEP)(Me)}$ , see *J. Am. Chem. Soc.* **1994**, *116*, 7189.

## Vitamin B<sub>12</sub> mechanism of action aided by sixth ligand coordination

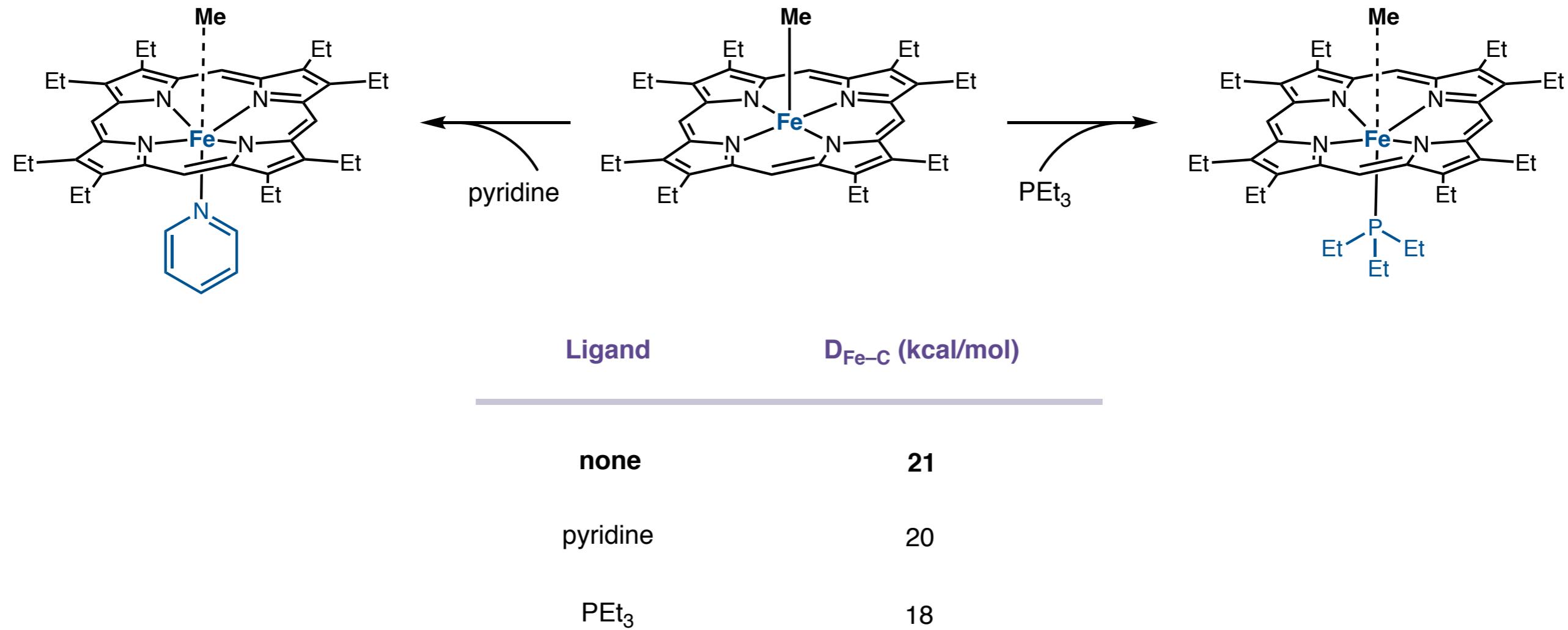


...this Co–C bond (either cyano, methyl or adenosyl)

Note: corrins are much easier to distort  
than porphyrins, BDE change is more dramatic

coordination of benzimidazole base at the axial site of  
Vitamin B<sub>12</sub> is proposed to stabilize...

*Iron–carbon bond strength also affected by axial ligation*



# *Outline*

## ***Characterization of metal porphyrin (alkyl) complexes***

I. molecular and electronic structure

II. metal-carbon bond strengths

III. electrochemical data

IV. synthesis and stability

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## ***Reactivity of metal porphyrin (alkyl) complexes***

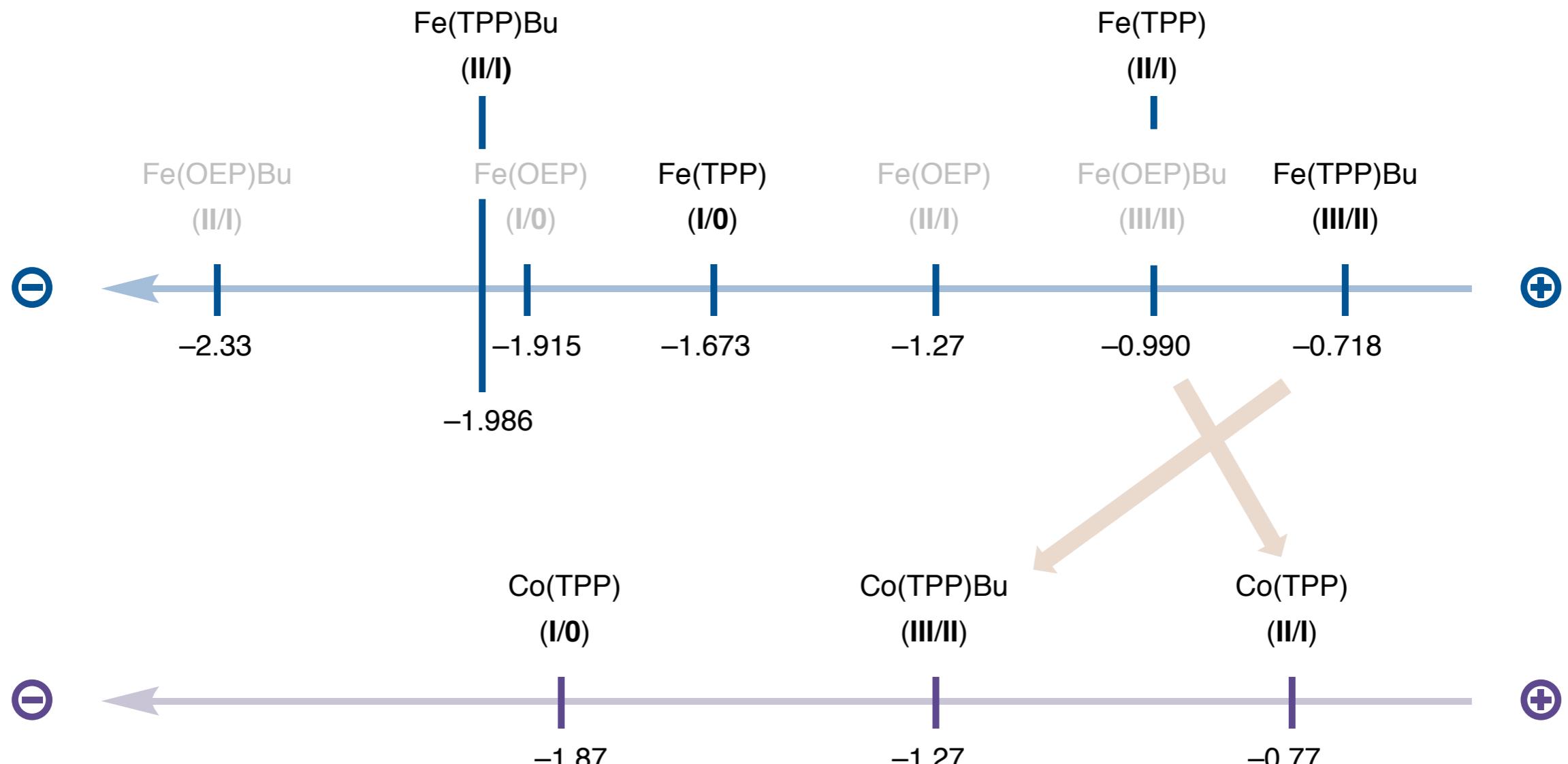
I. photolysis of metal-ligand bonds in porphyrin complexes (*precatalyst activation*)

A. photochemistry of metal porphyrins

II. alkylation of iron porphyrins by nucleophilic displacement (*substrate activation*)

III. the S<sub>H</sub>2 mechanism and metal porphyrins (*bond formation*)

# Electrochemical data for iron and cobalt porphyrin complexes



OEP = octaethylporphyrin

TPP = tetraphenylporphyrin

Why is there a change in order of redox couples?

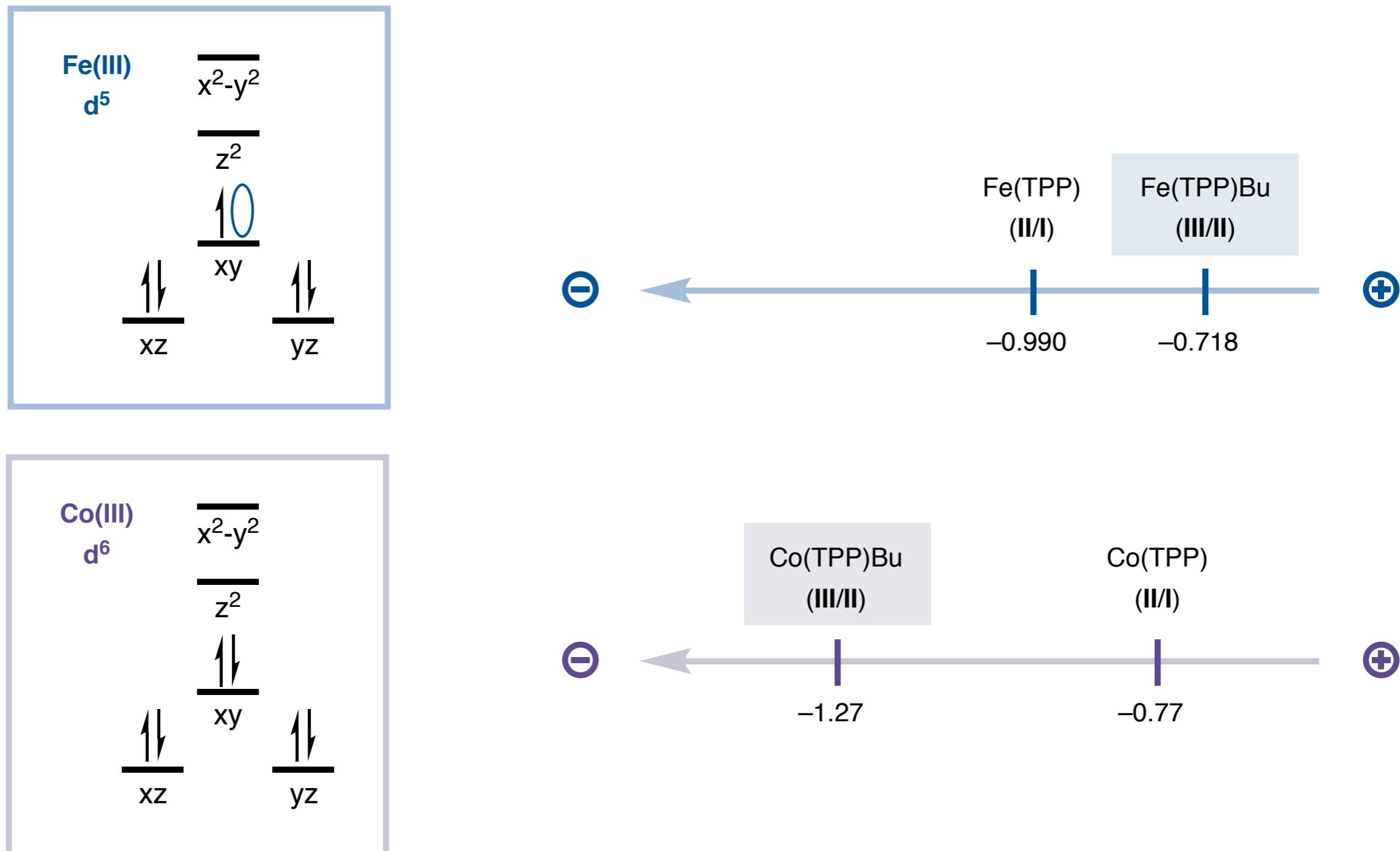
Lexa, D.; Savéant, J.-M.; Wang, D. L. *Organometallics* **1986**, *5*, 1428.

Qiu, A.; Sawyer, D. T. *J. Porphyr. Phthalocyanines* **1997**, *1*, 125.

Lexa, D.; Mispelter, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1981**, *103*, 6806.

\*all values were measured in DMF at 20 °C in V vs. SCE using a glassy carbon electrode

# *Electrochemical data for iron and cobalt porphyrin complexes*



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## ***Characterization of metal porphyrin (alkyl) complexes***

I. molecular and electronic structure

II. metal-carbon bond strengths

III. electrochemical data

IV. synthesis and stability

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## ***Reactivity of metal porphyrin (alkyl) complexes***

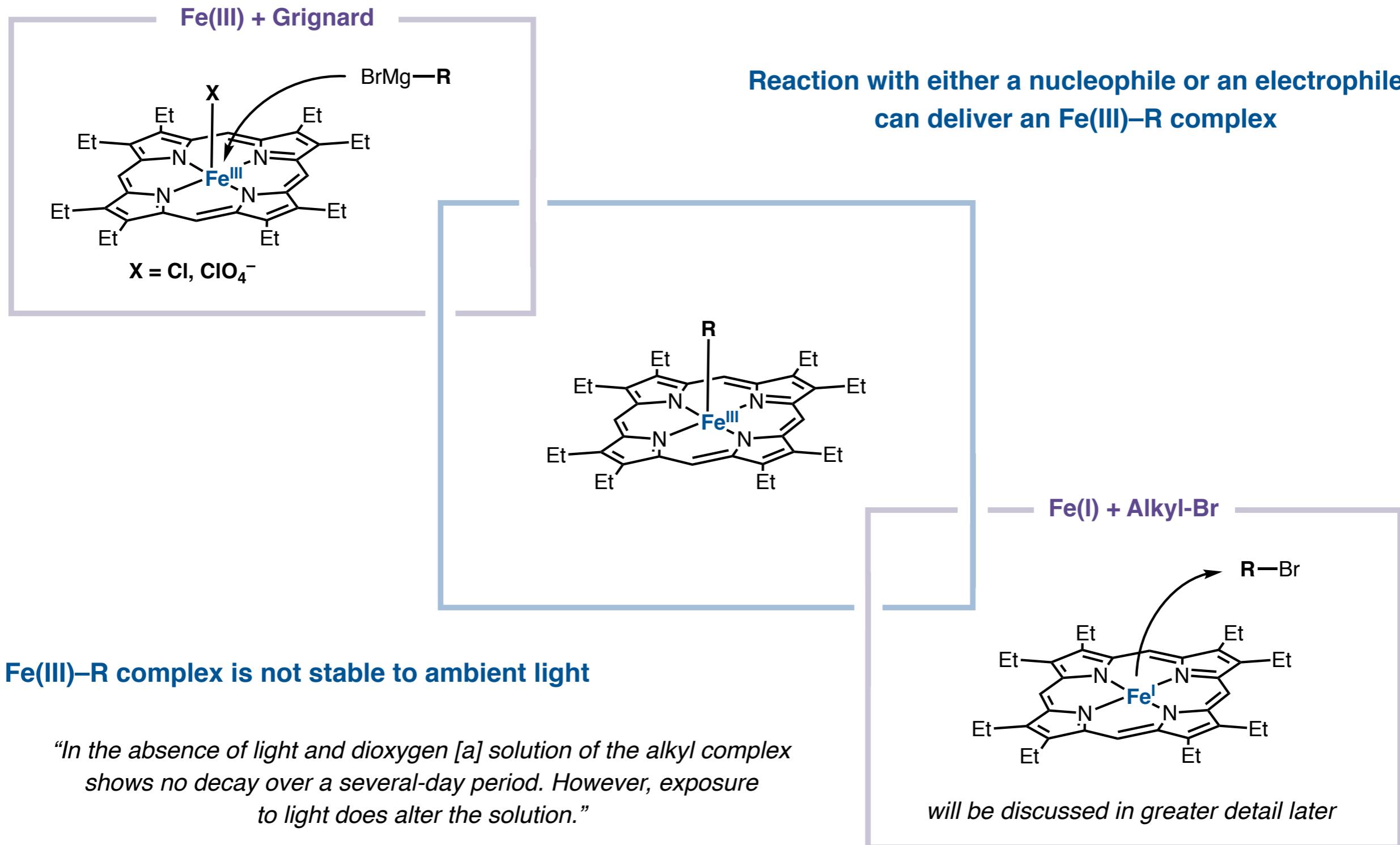
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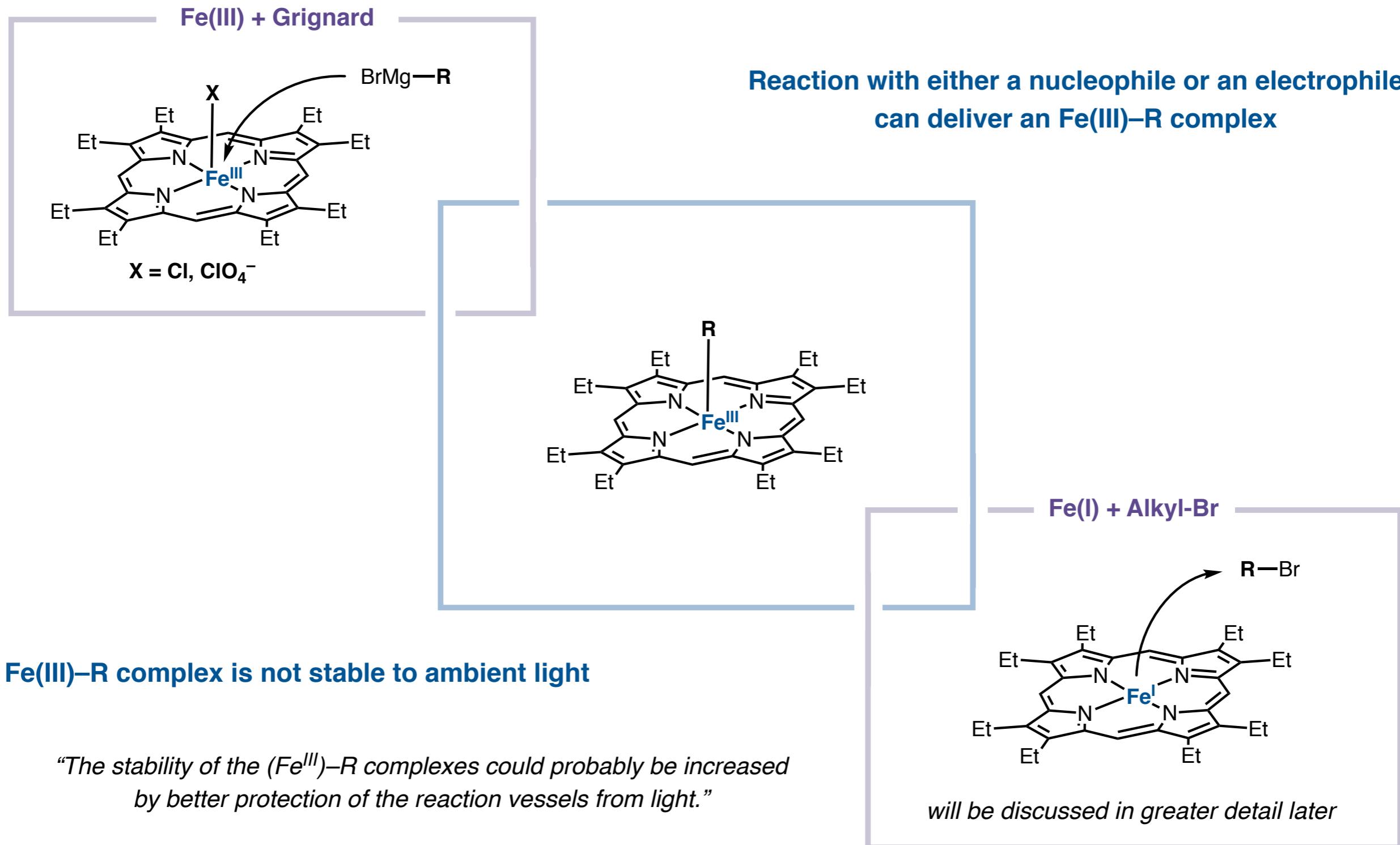
# Synthesis and stability of Fe–alkyl porphyrin complexes



Arasasingham, R. D.; Balch, A. L.; Corman, C. R.; Latos-Grazynski, L. *J. Am. Chem. Soc.* **1989**, *111*, 4357.

Lexa, D.; Mispelter, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1981**, *103*, 6806.

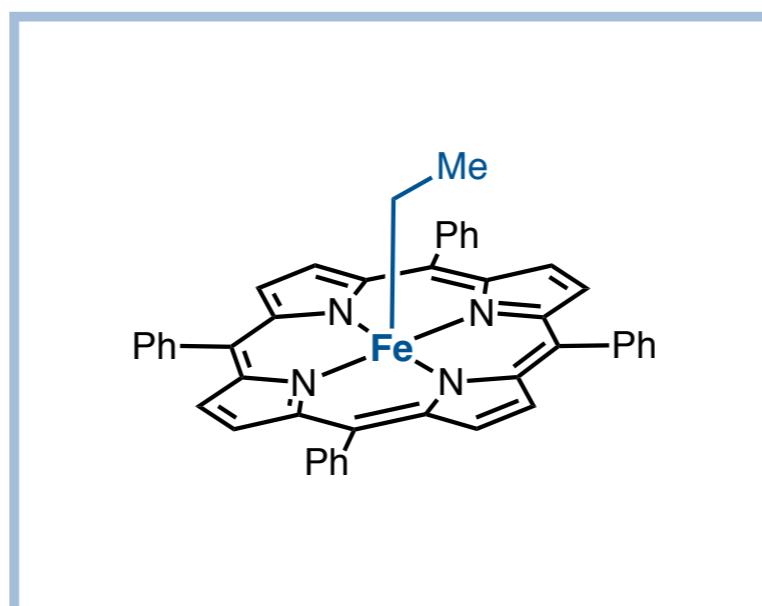
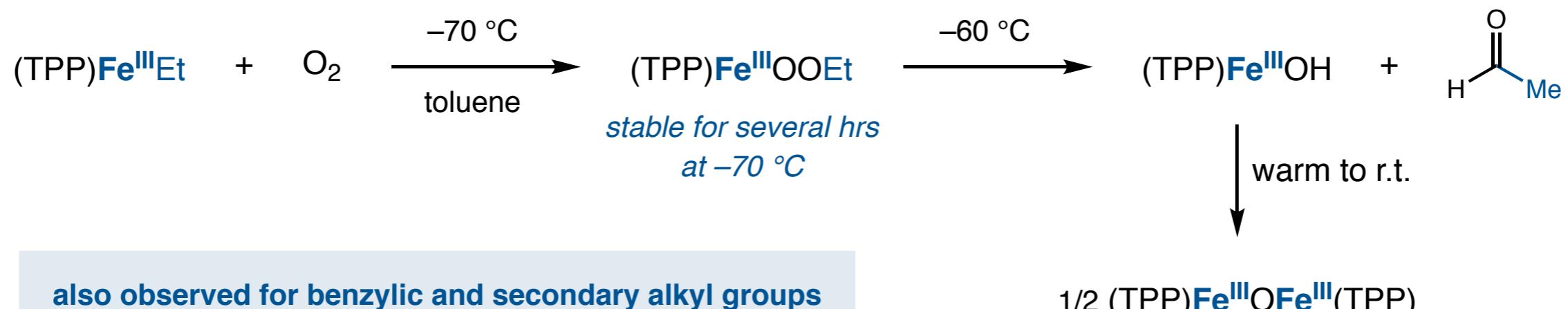
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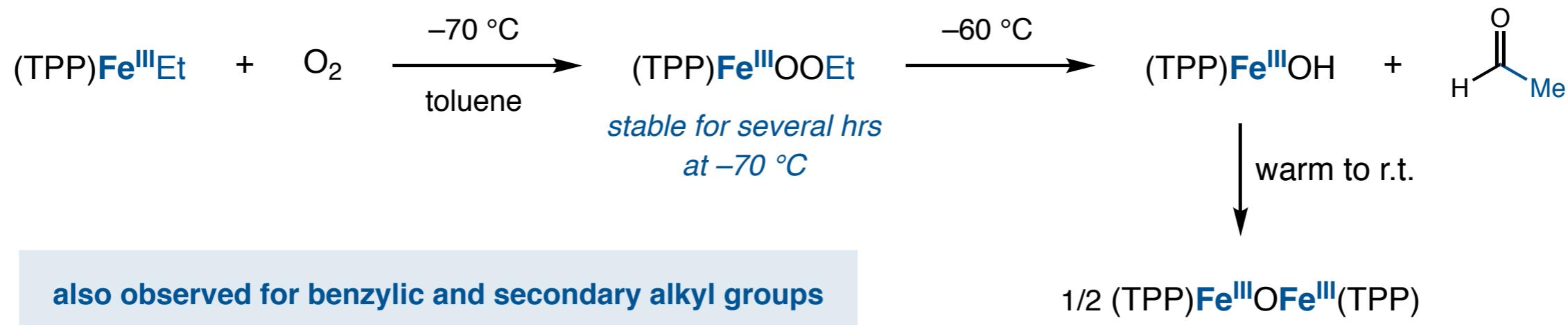
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## *O<sub>2</sub>* insertion into the Fe(III)–Carbon bond

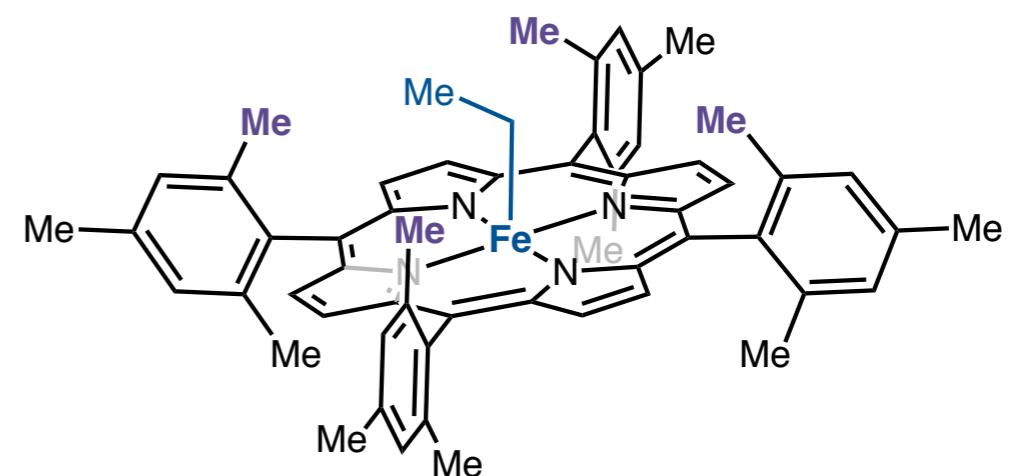


## *O<sub>2</sub>* insertion into the Fe(III)–Carbon bond



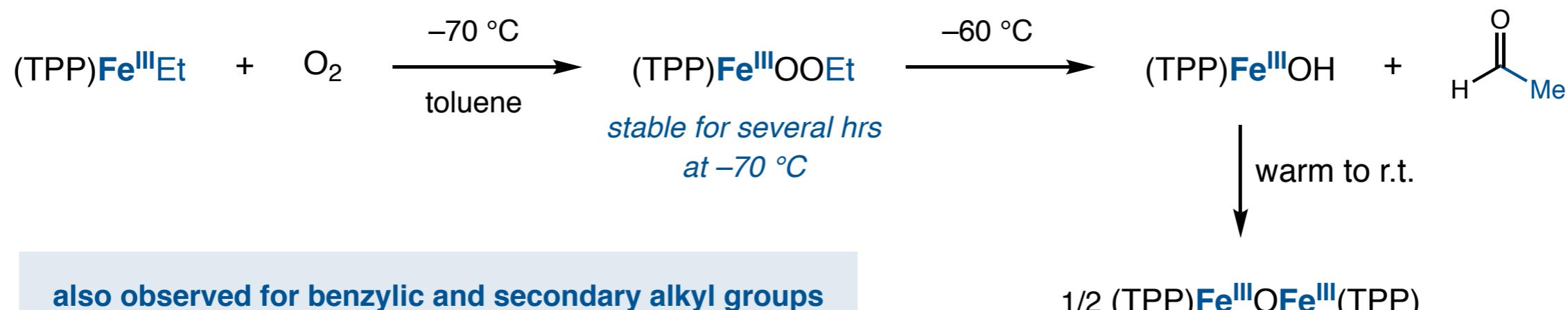
inhibited by...

- sterically encumbered porphyrins



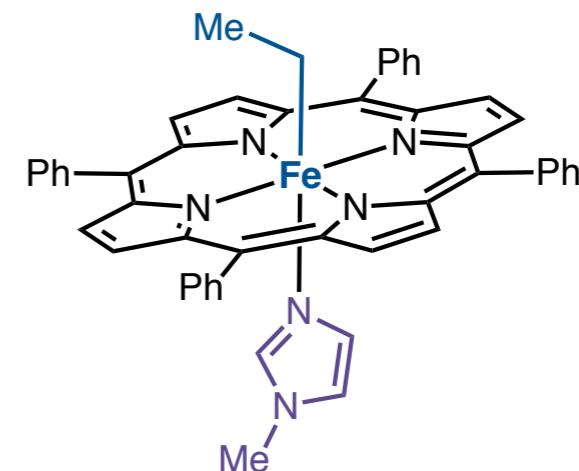
dioxygen insertion observed at -50 °C

## *O<sub>2</sub>* insertion into the Fe(III)–Carbon bond



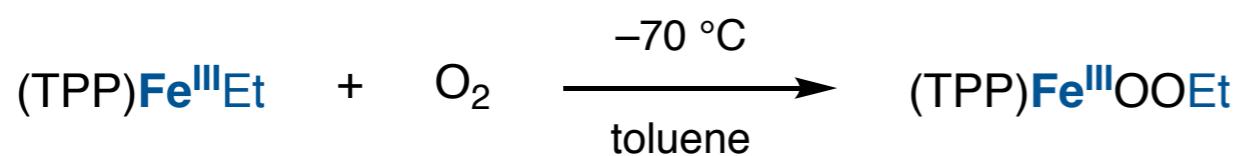
inhibited by...

- sterically encumbered porphyrins
- coordination at the sixth ligand site



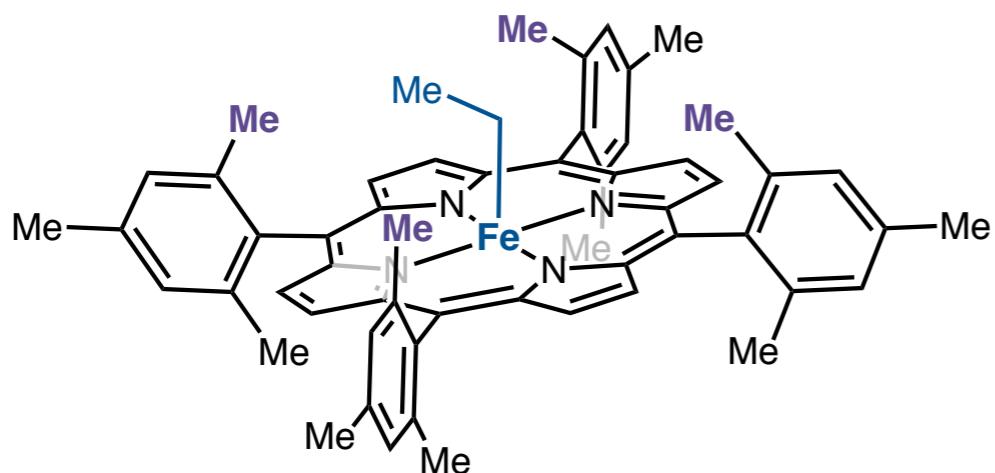
dioxygen insertion observed at -30 °C

## Does $O_2$ insertion proceed through Fe–C bond homolysis?

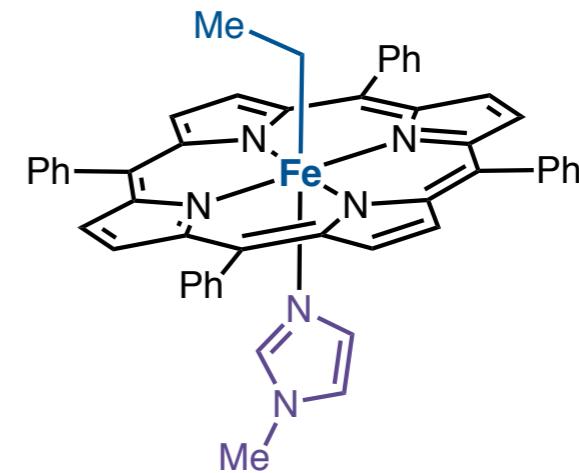


**Two possible mechanisms:**

1. Fe–C bond homolysis and  $O_2$  addition
2.  $O_2$  attack and insertion into Fe–C bond



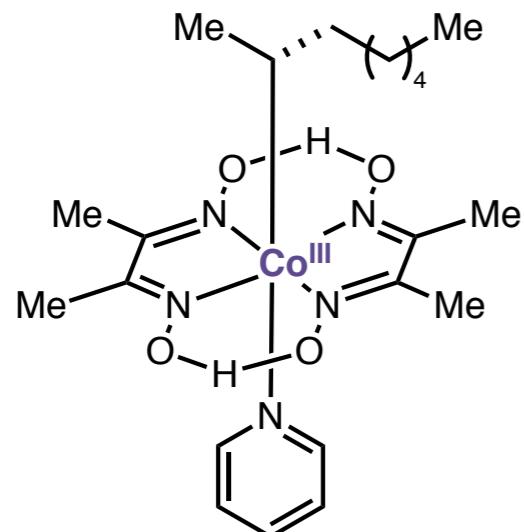
if Fe–C bond homolysis were involved,  
steric effect *would be minimal*



imidazole weakens Fe–C bond,  
but *inhibits reaction with O<sub>2</sub>*

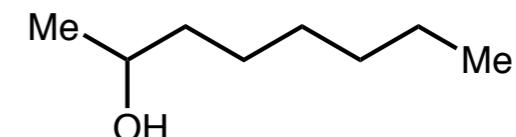
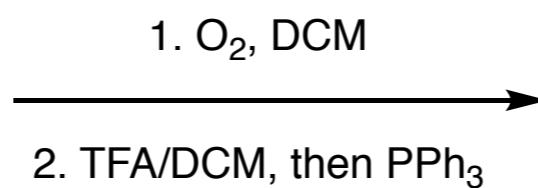
both experimental observations support a *thermal* mechanism that *does not include Fe–C bond homolysis*

## *Comparison to the alkylcobaloxime system*



$\text{RCo}(\text{dmgH})_2(\text{pyr})$

common vitamin  $\text{B}_{12}$  model complex



**racemic alcohol product**

diagnostic of homolytic Co–C cleavage

A brief footnote:

*under photochemical conditions, bond homolysis is a facile process for both Fe and Co systems*

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I. photolysis of metal-ligand bonds in porphyrin complexes (*precatalyst activation*)

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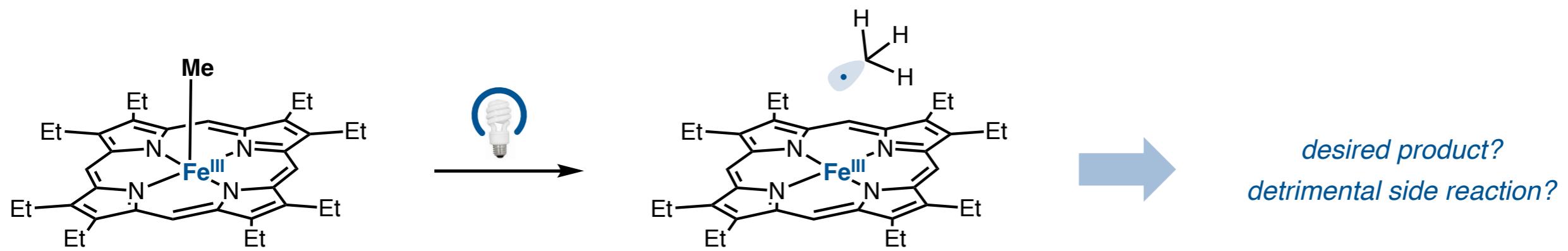
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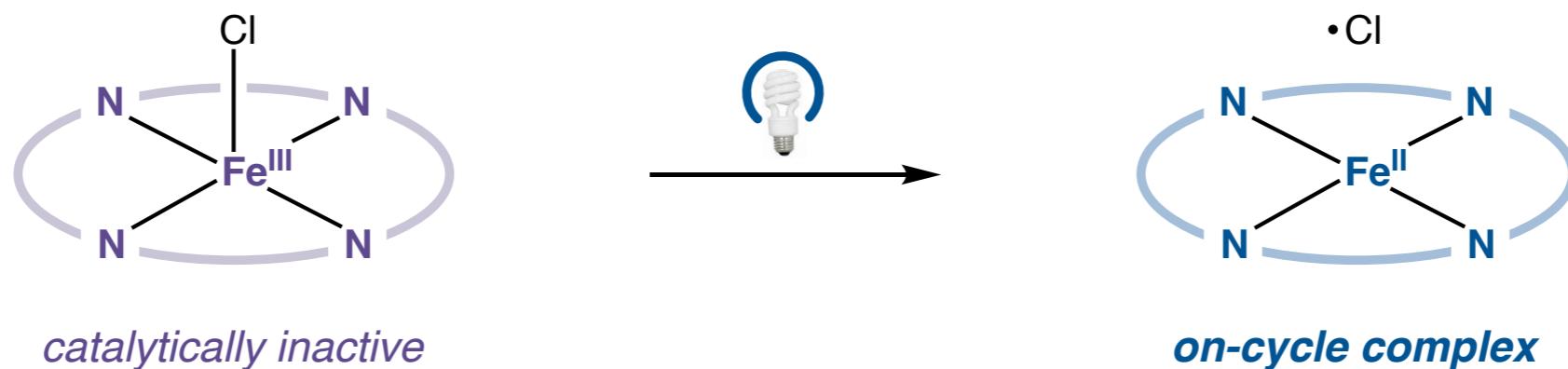
III. the S<sub>H</sub>2 mechanism and metal porphyrins (*bond formation*)

## *Relevance of photolysis of Fe–alkyl and Fe–halide bonds*

### ■ Possible intermediate step in Fe-mediated cross-coupling

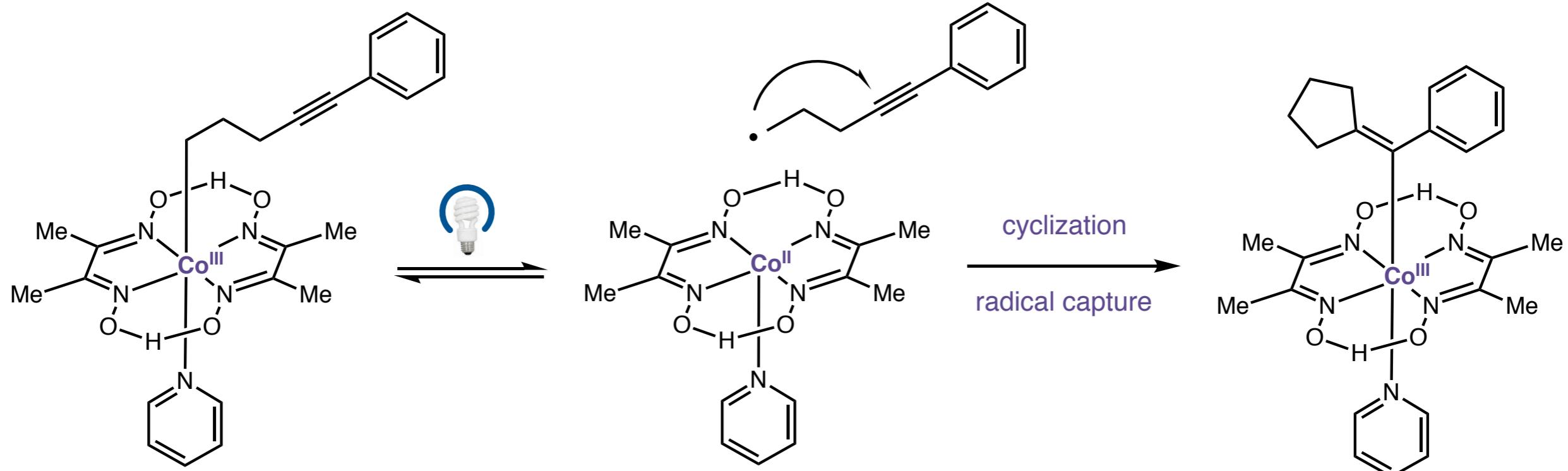


### ■ Activation of precatalyst $\text{Fe}^{\text{III}}(\text{OEP})\text{Cl}$

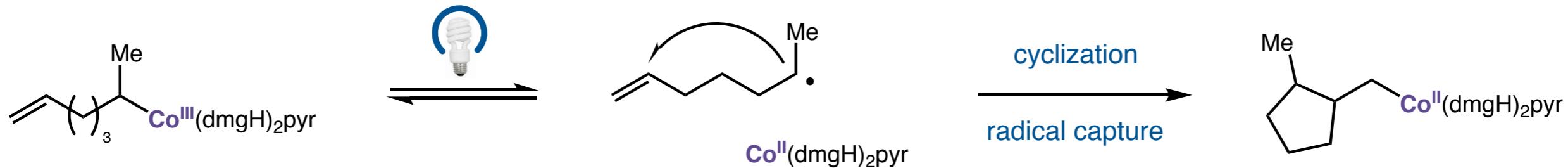


# Radical clocks to probe metal–carbon bond photolysis

rearrangement to yield vinylic secondary benzylic radical



rearrangement to generate new primary radical



## *A (brief) introduction to porphyrin photochemistry*

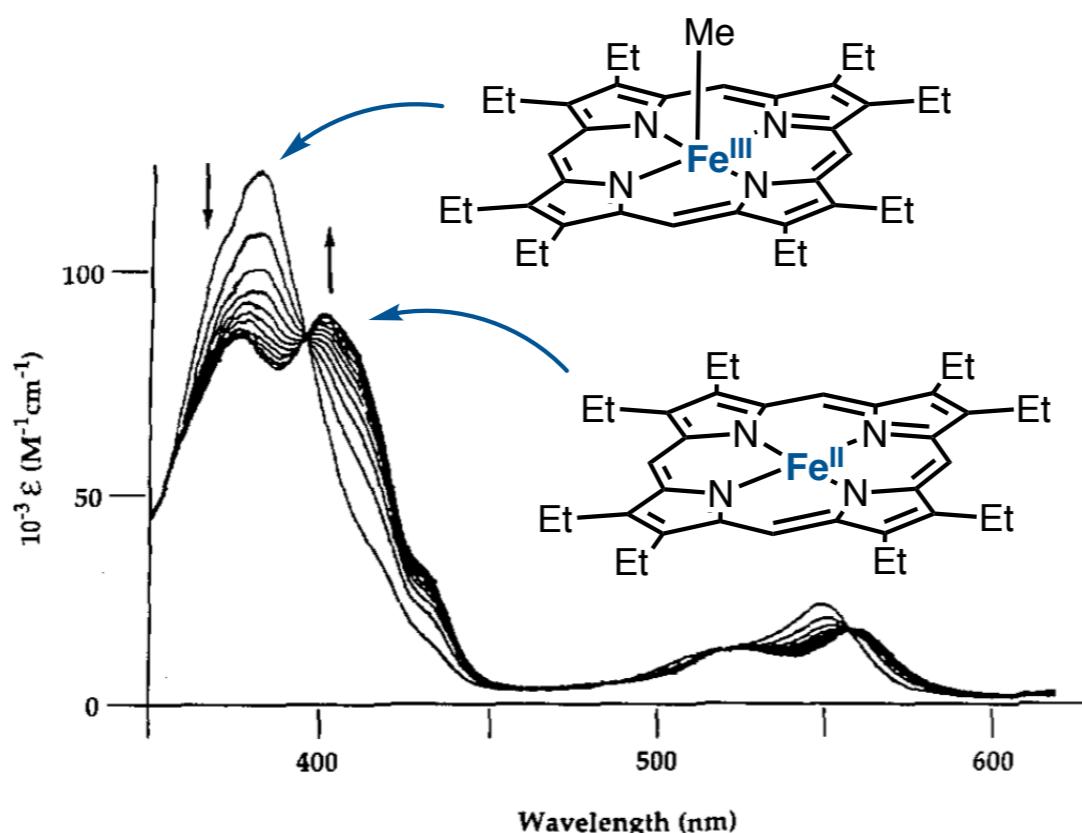
**Where and how strongly do these metal porphyrin complexes absorb?**

---

**Why does visible light irradiation result in Fe–C bond homolysis?**

## Comparisons between Fe(OEP) and Fe(OEP)(Me) UV-Vis absorption

Monitoring the progress of the following reaction by UV-Vis...



Reactions involving porphyrins  
are often monitored  
by UV-Vis

Fig. 1. Electronic spectral changes accompanying the thermolysis of  $\text{Fe}(\text{OEP})\text{CH}_3 (5.0 \times 10^{-5} \text{ M})$  in the presence of  $\text{Ph}_3\text{SnH} (1.0 \times 10^{-3} \text{ M})$  in benzene at  $50^\circ\text{C}$ . Spectra were recorded at 60 s intervals.

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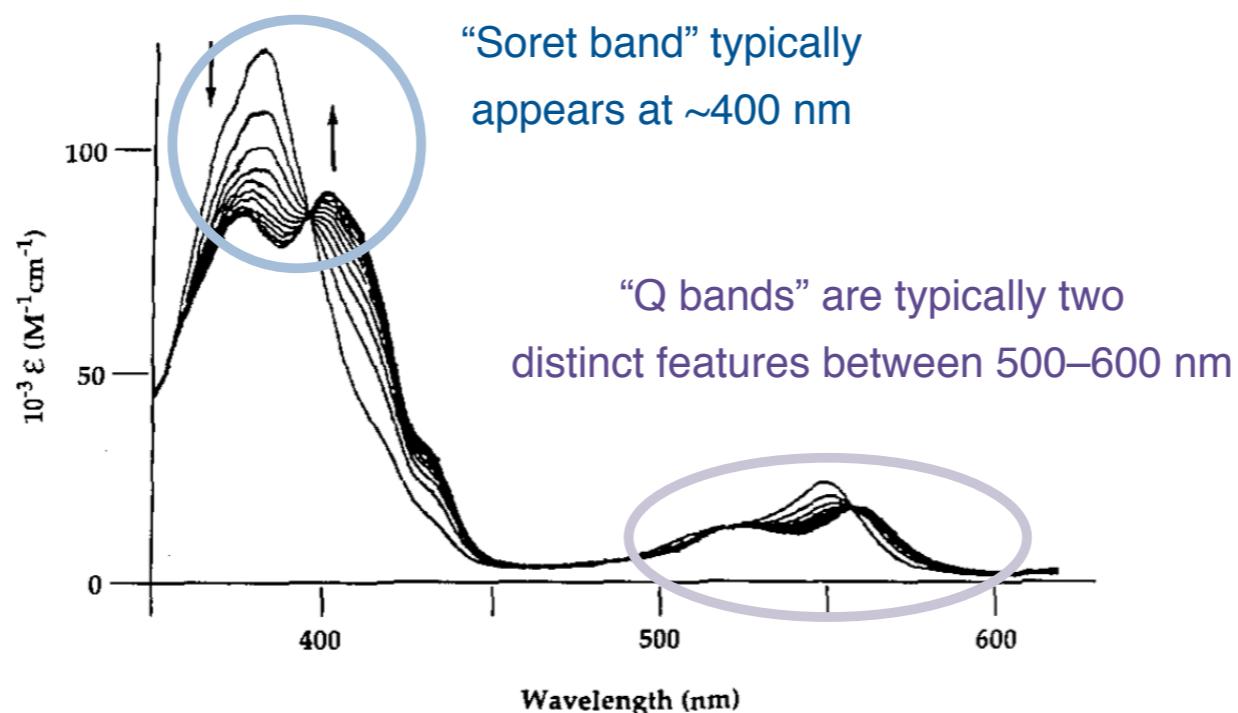
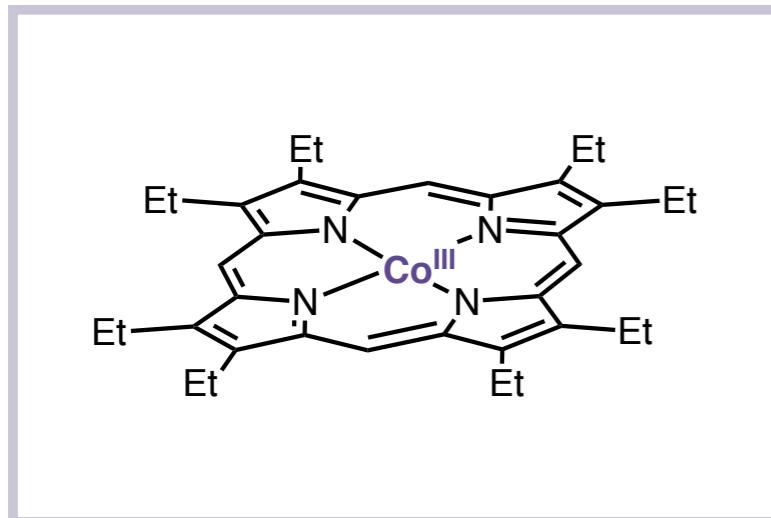
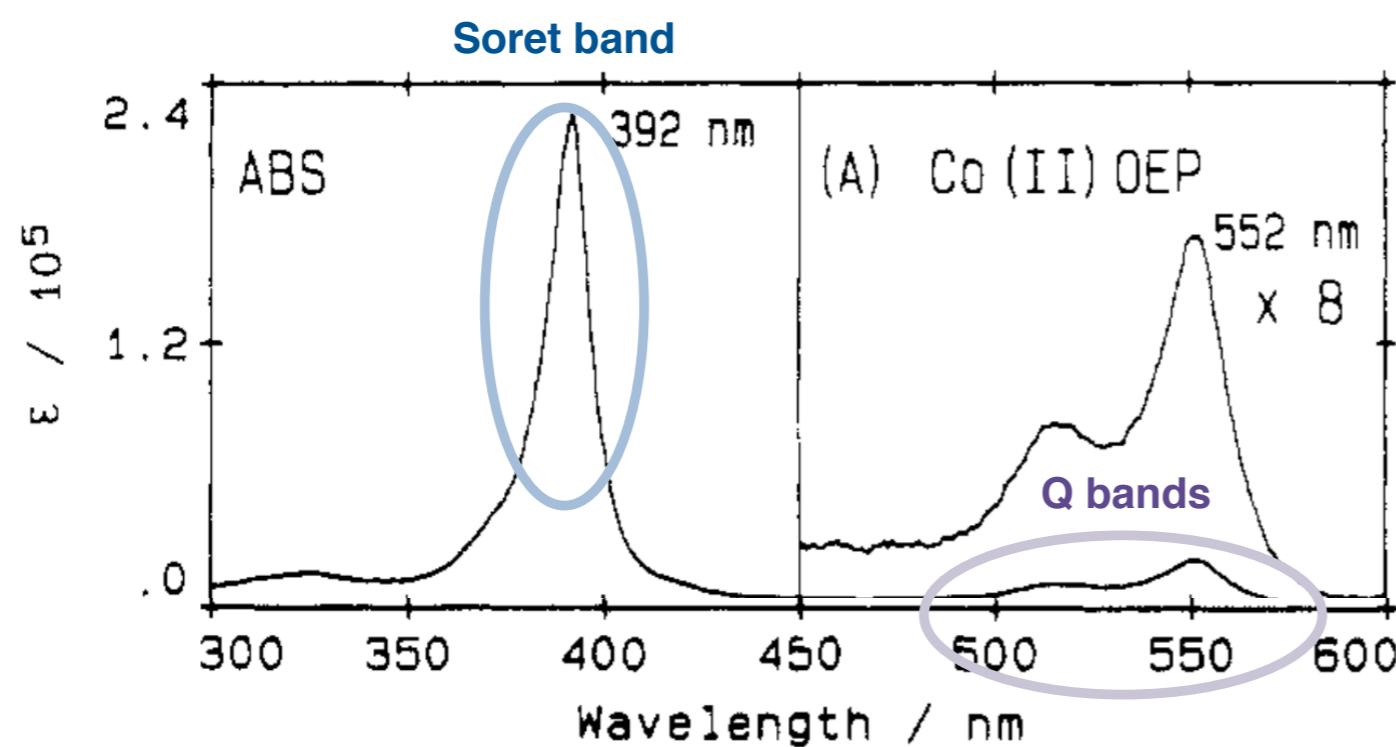


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## UV-Vis absorption spectra for Co(OEP) complexes

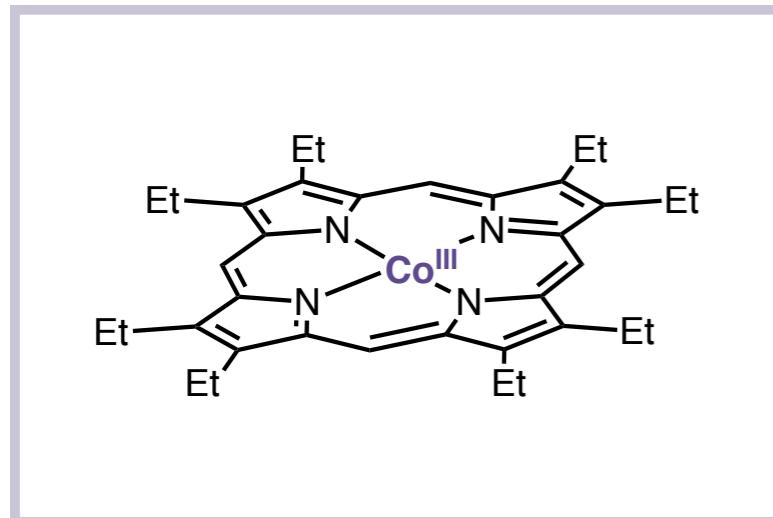


same spectral features as Fe complexes ■ absorption bands are **blue shifted**

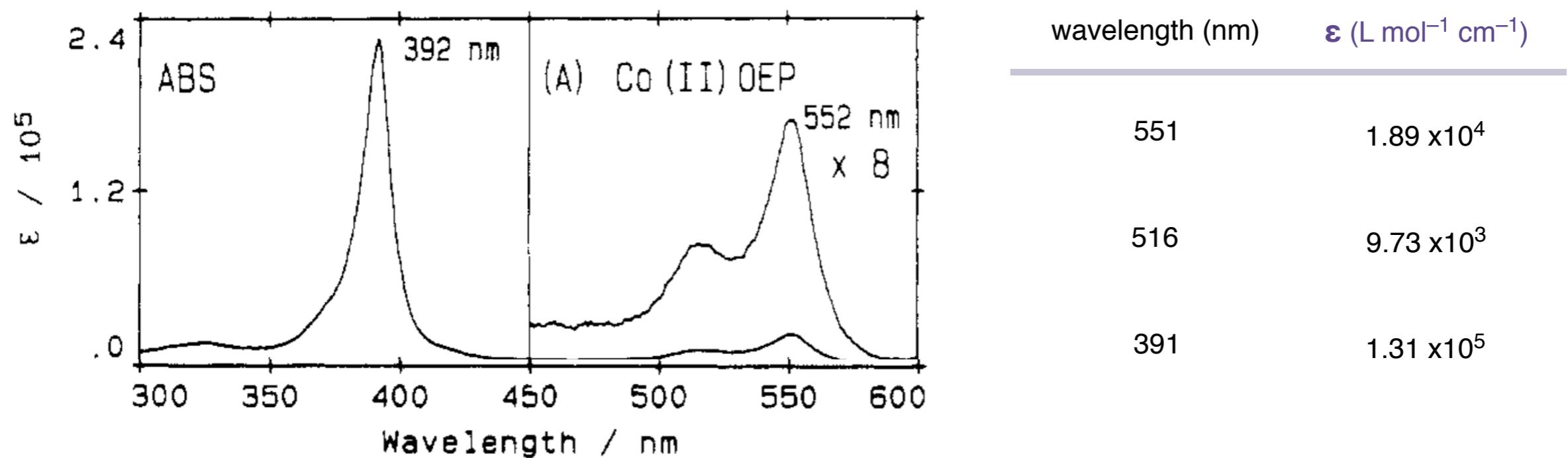


for R = Me, Et, and 2-propionate  
UV-Vis spectrum remains  
essentially unchanged

## UV-Vis absorption spectra for Co(OEP) complexes

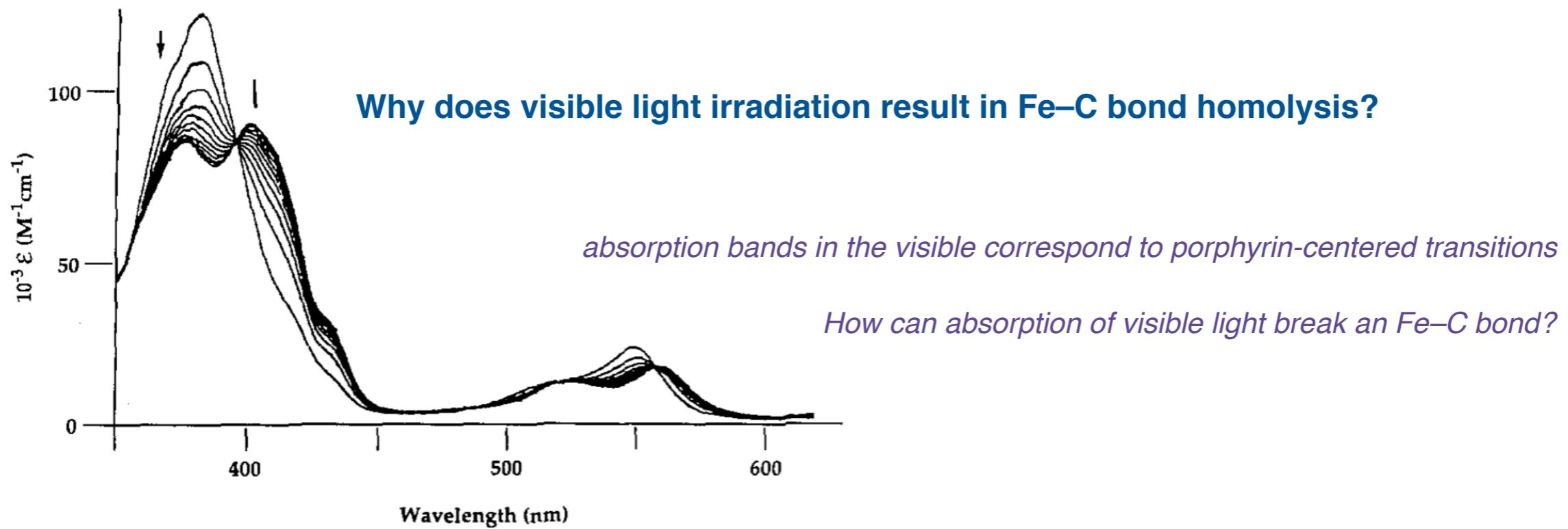


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# *A (brief) introduction to porphyrin photochemistry*

**Where and how strongly do these metal porphyrin complexes absorb?**

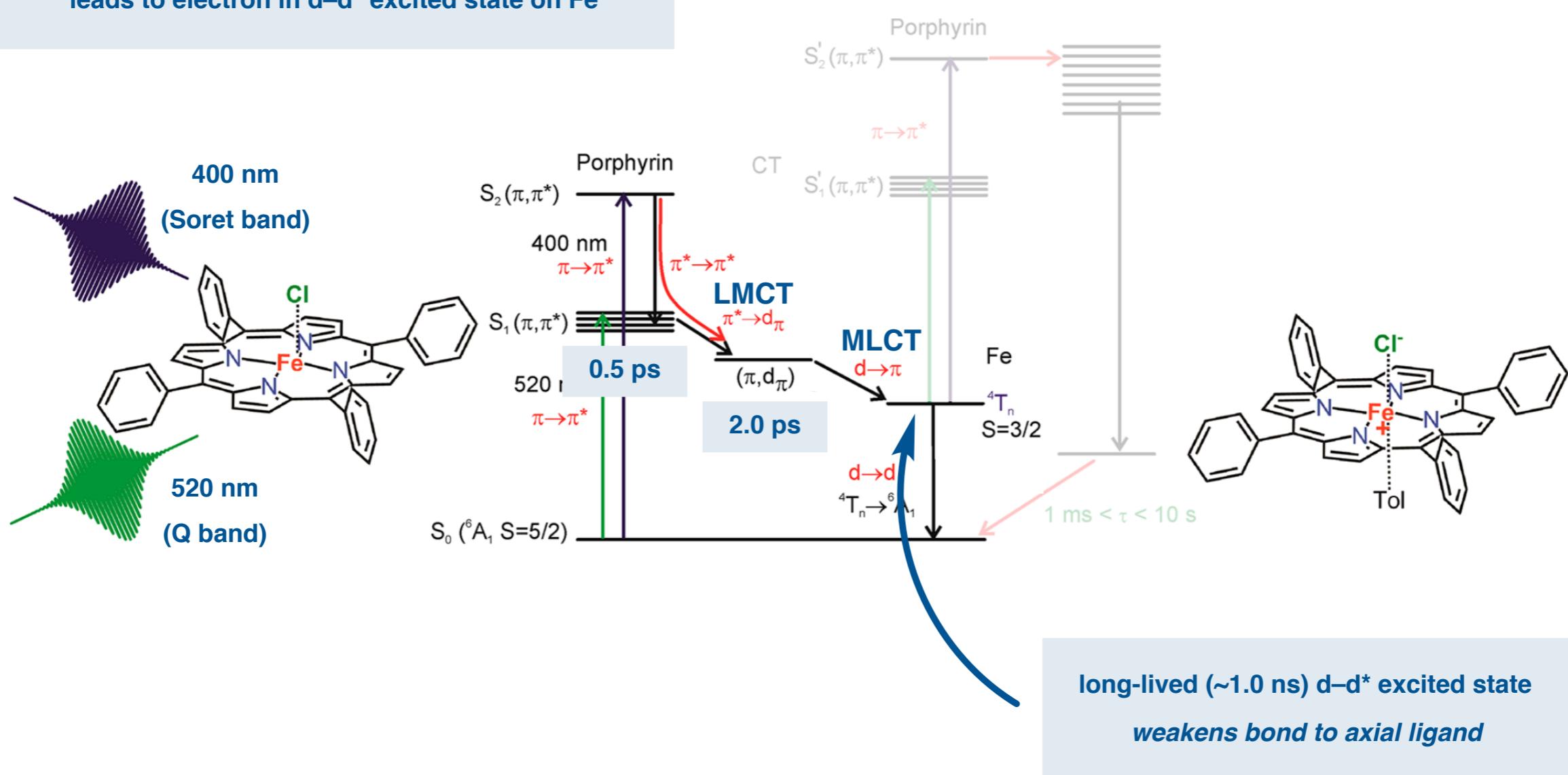


# Ultrafast transient absorption maps energy cascade in excited Fe porphyrins

although initial excited state is  $\pi-\pi^*$

internal conversion and LMCT/MLCT sequence

leads to electron in d-d\* excited state on Fe



# *Outline*

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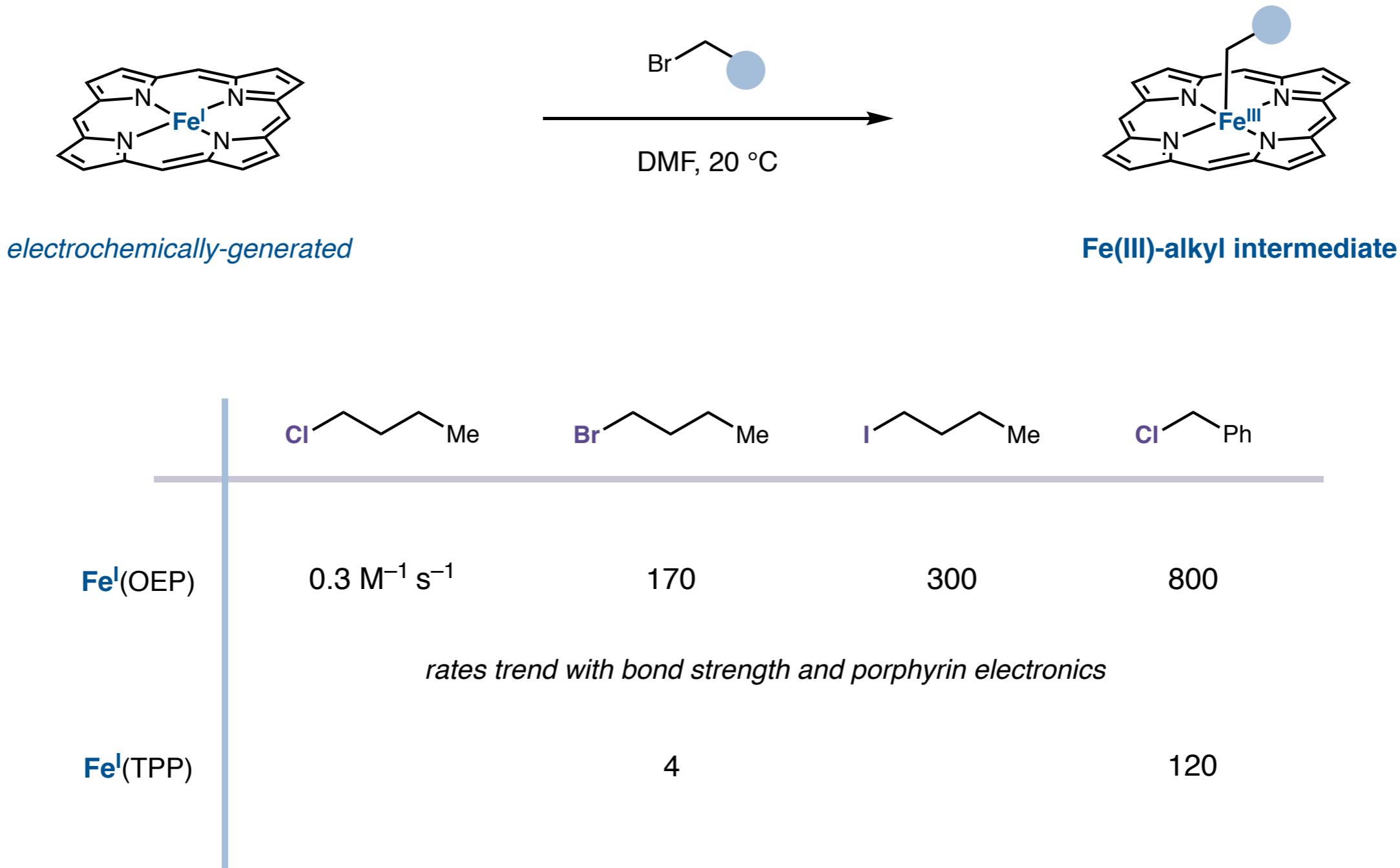
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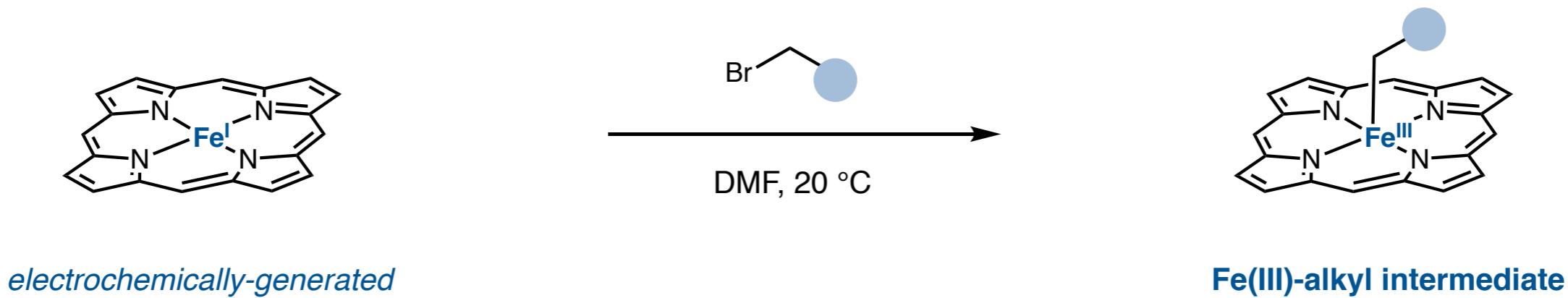
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## *Rate constants for iron porphyrin alkylation with primary halides*

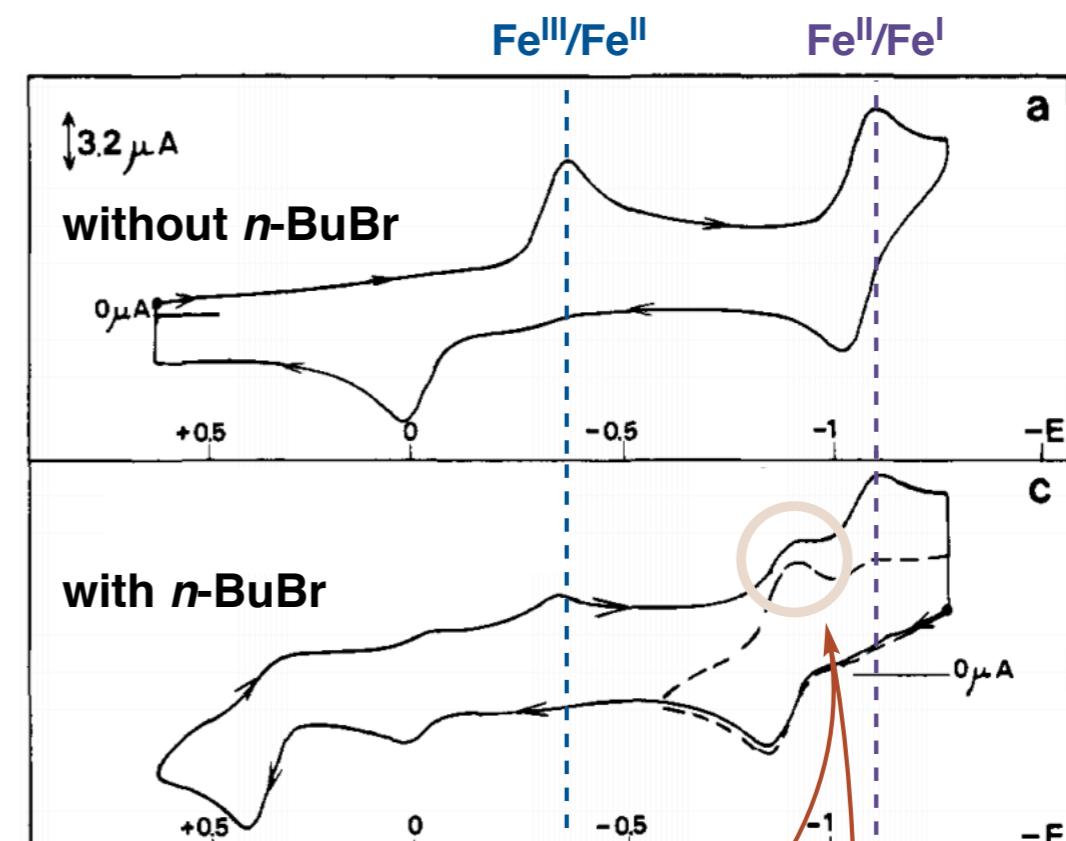
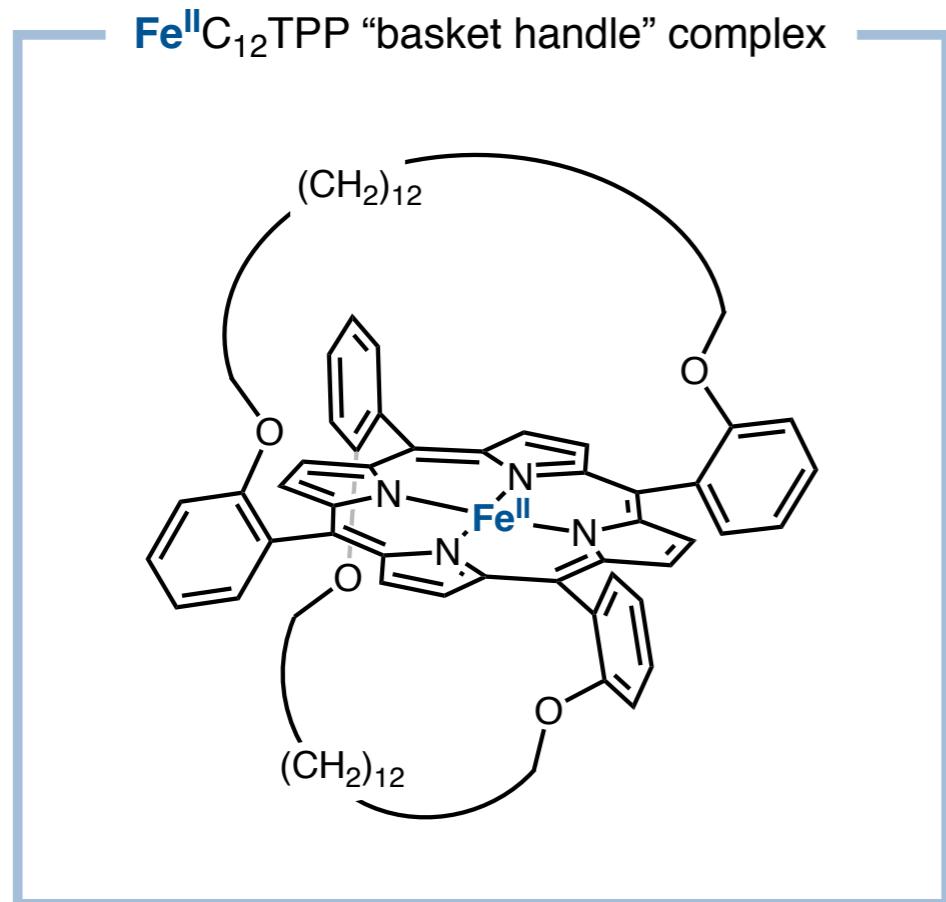


## *Rate constants for iron protoporphyrin alkylation with primary halides*

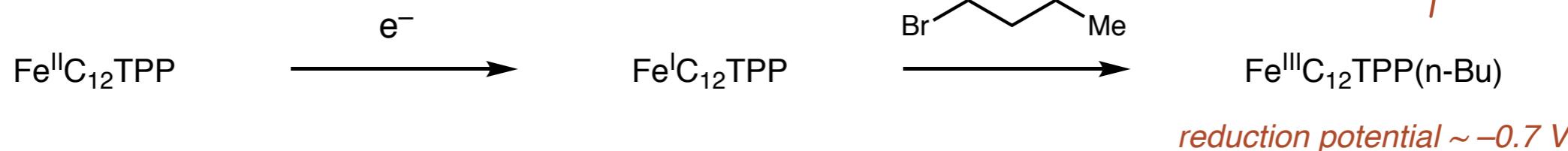


How do we know that Fe(I) is activating the bromide?

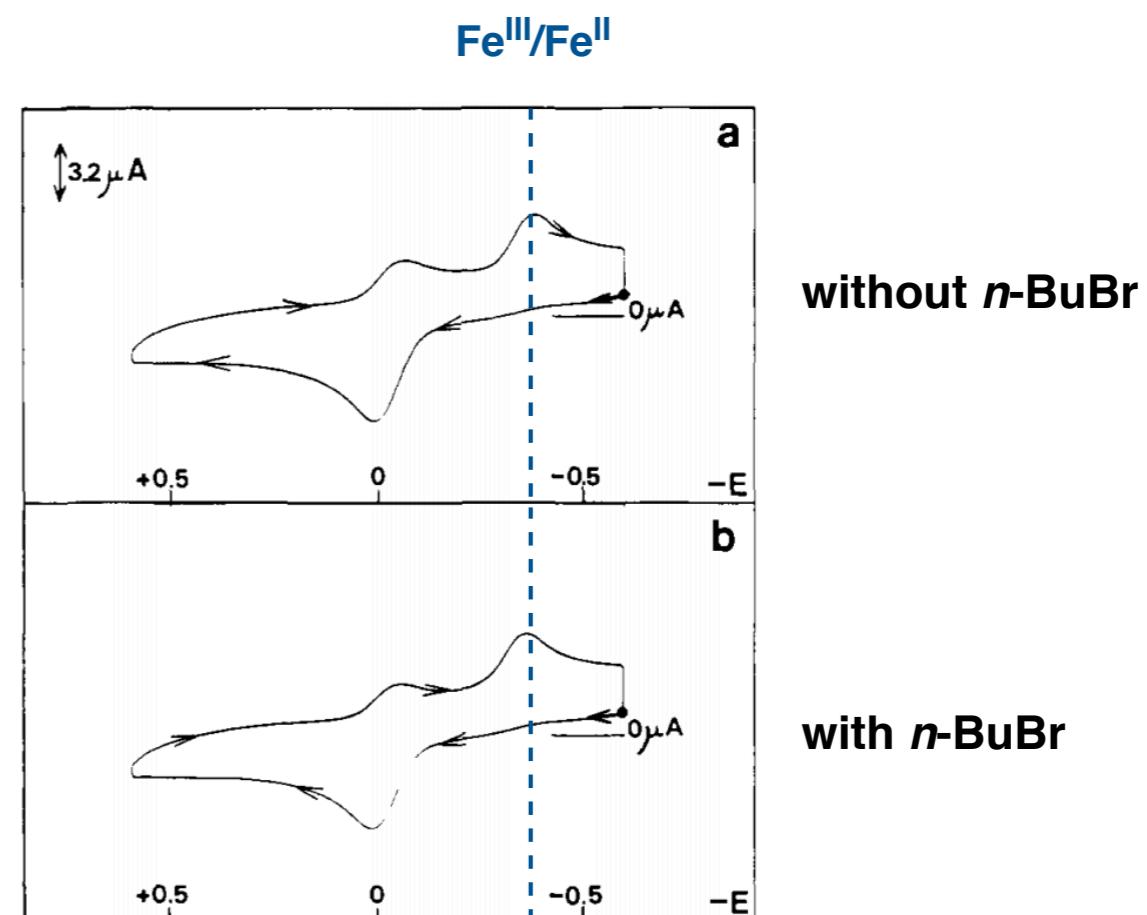
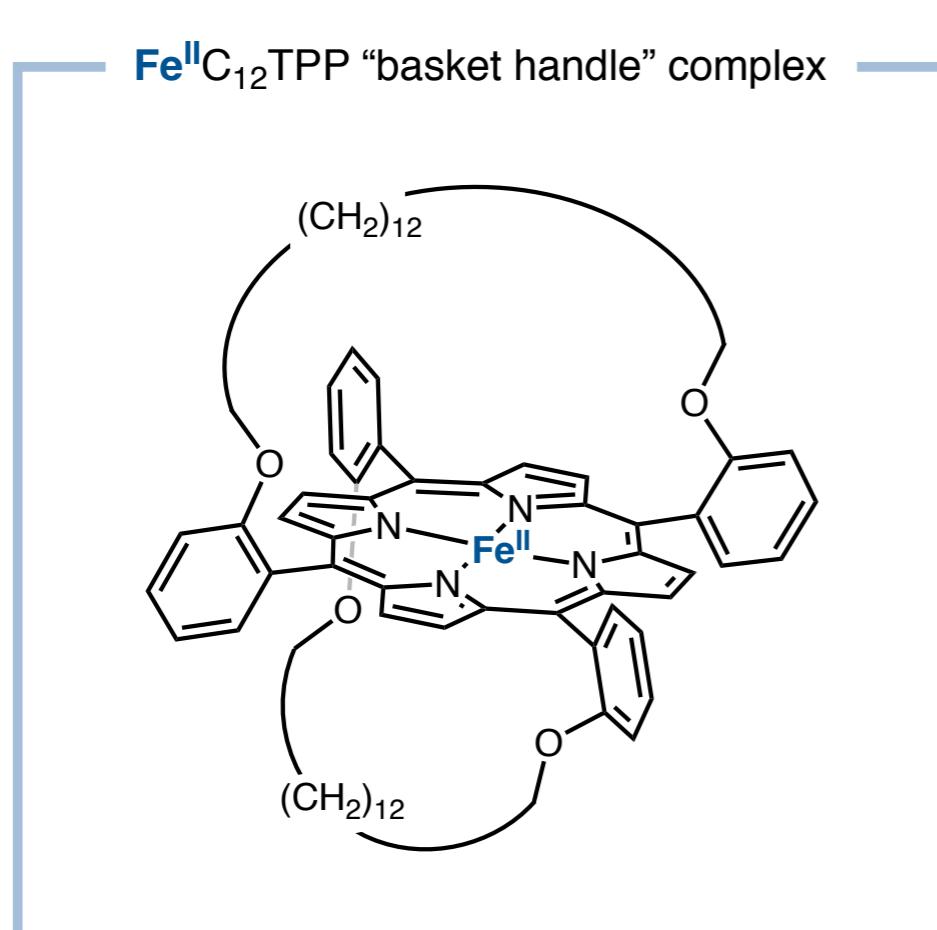
*Cyclic voltammetry provides insight into reactive Fe oxidation state*



new reversible couple appears just before Fe<sup>II</sup>/Fe<sup>I</sup> couple  
other ligands (OEP, TPP) behaved similarly

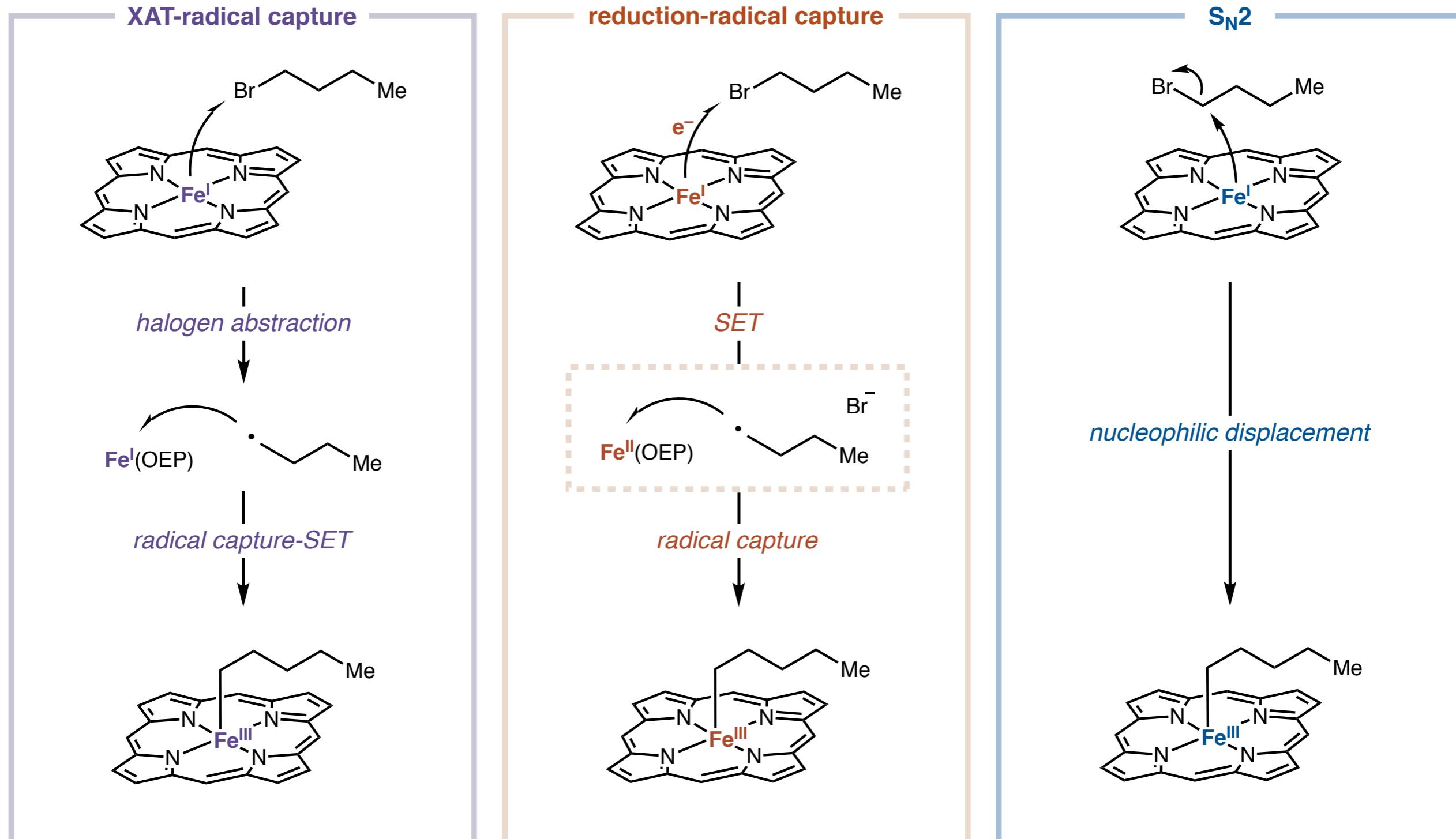


## Cyclic voltammetry provides insight into reactive Fe oxidation state



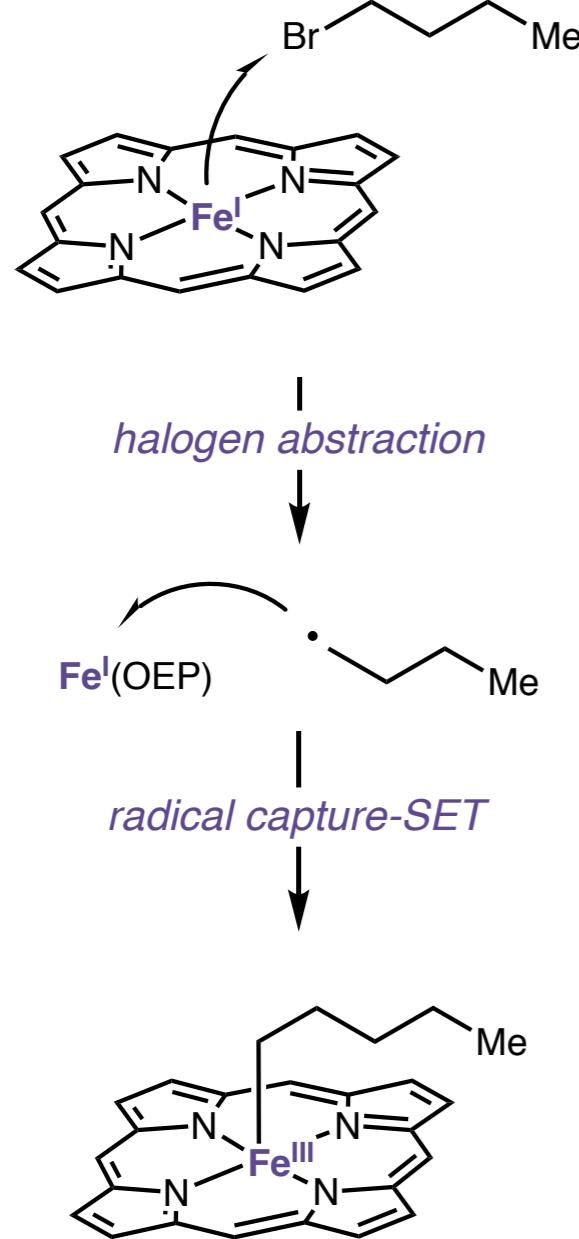
CV the same regardless of presence of *n*-BuBr, indicating no reaction between Fe(II) or Fe(III) and alkyl bromides

## Possible mechanisms of alkyl bromide activation by Fe(I) porphyrin



# *Halogen abstraction-radical capture by Fe(I)*

## XAT-radical capture



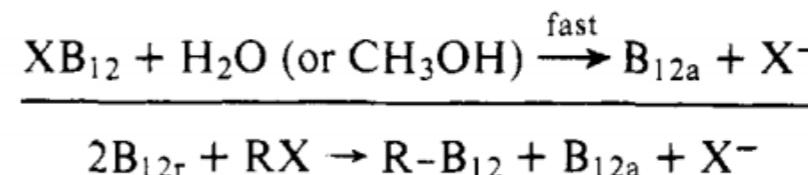
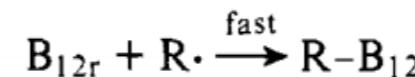
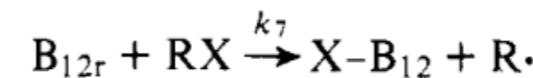
would allow 1°, 2° or 3° bromides to interact with Fe

## Arguments in favor:

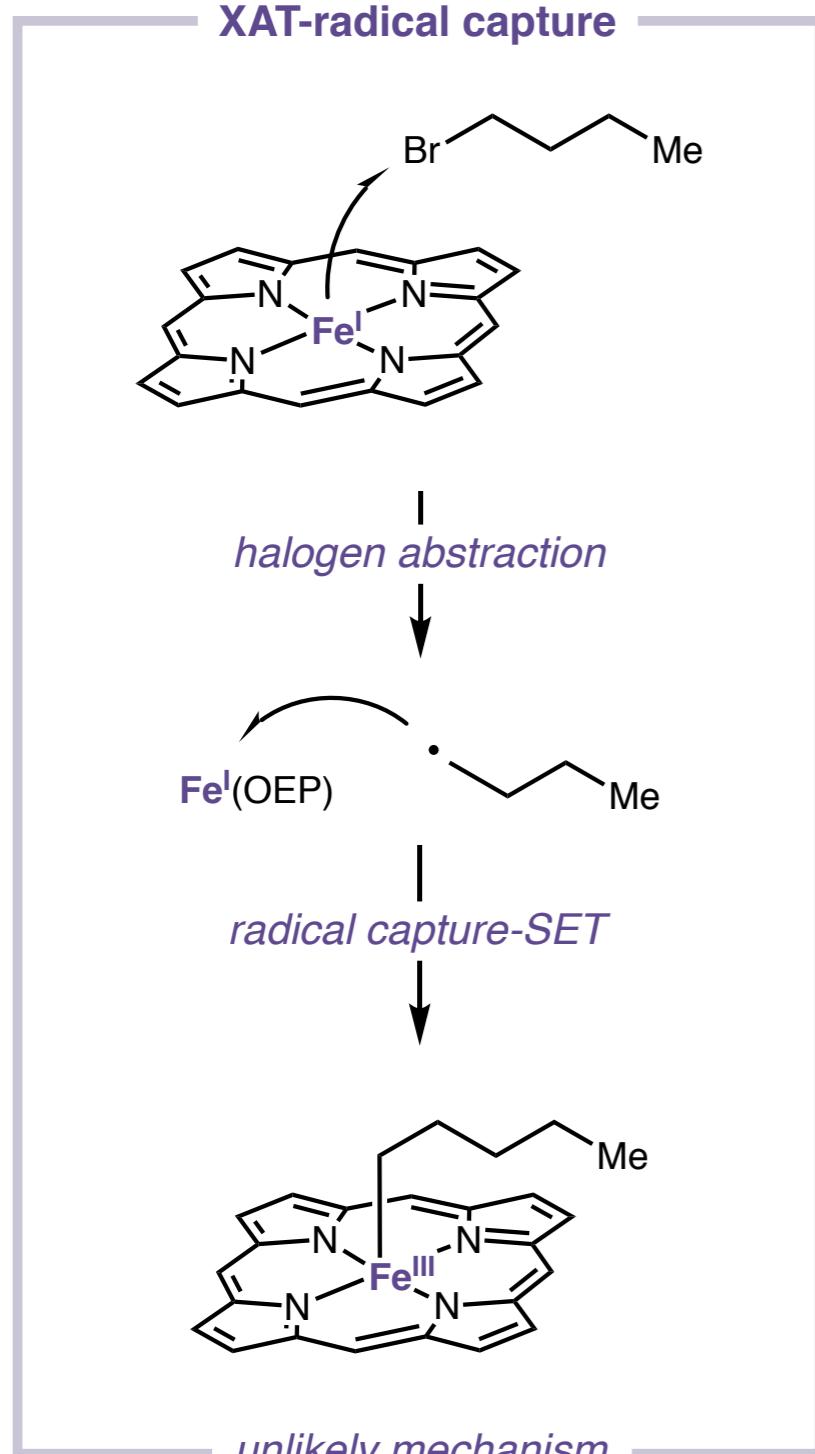
### 1. Fe(I) higher radical affinity than Fe(II)

consistent with Fe(II) being unreactive towards Alkyl-Br

### 2. Isoelectronic Co(II) in Vitamin B<sub>12</sub> operates through this mechanism



# *Halogen abstraction-radical capture by Fe(I)*

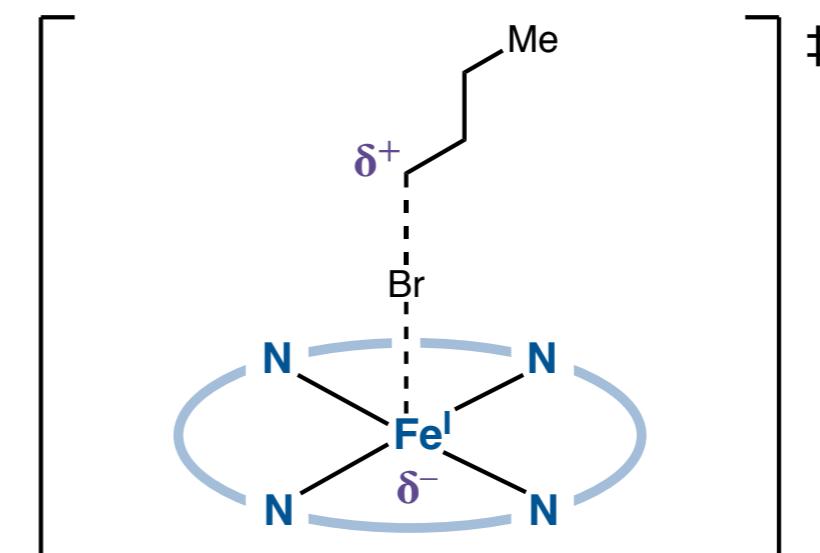


would allow 1°, 2° or 3° bromides to interact with Fe

— Argument against: —

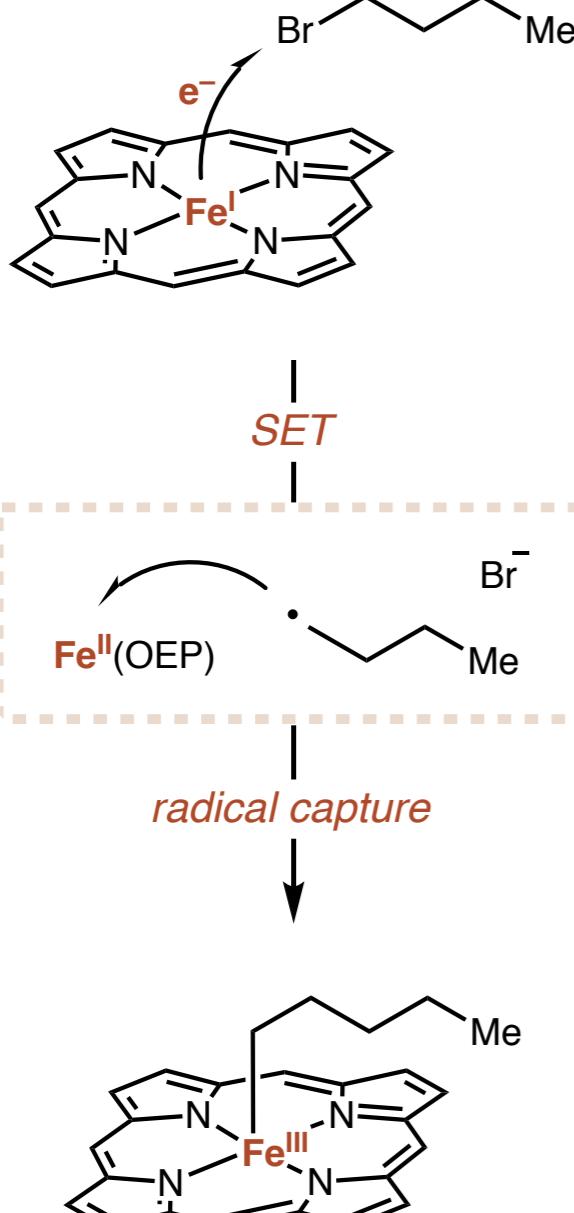
low affinity of iron for halide abstraction

polarity-mismatched transition state



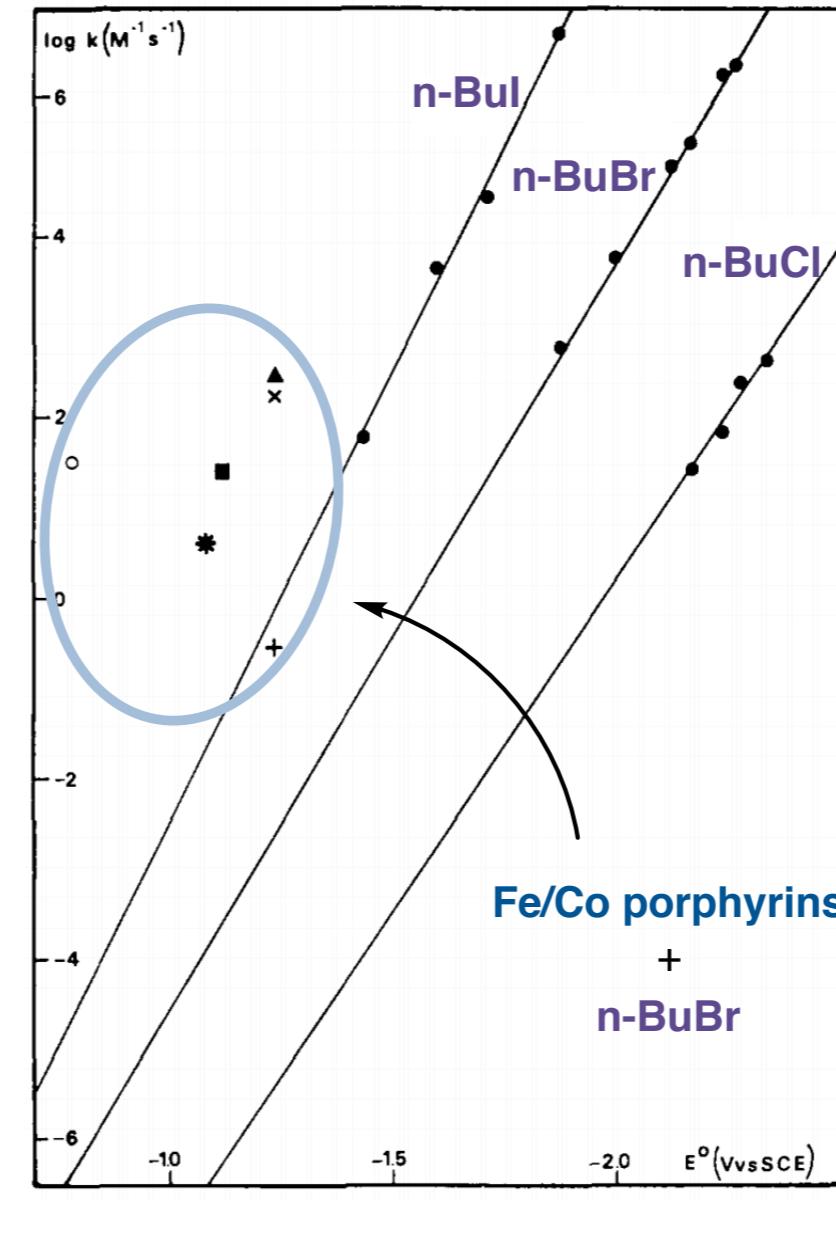
# *Direct reduction and in-cage radical capture by Fe*

## reduction-radical capture



*unlikely mechanism*

rate of reaction with primary bromide

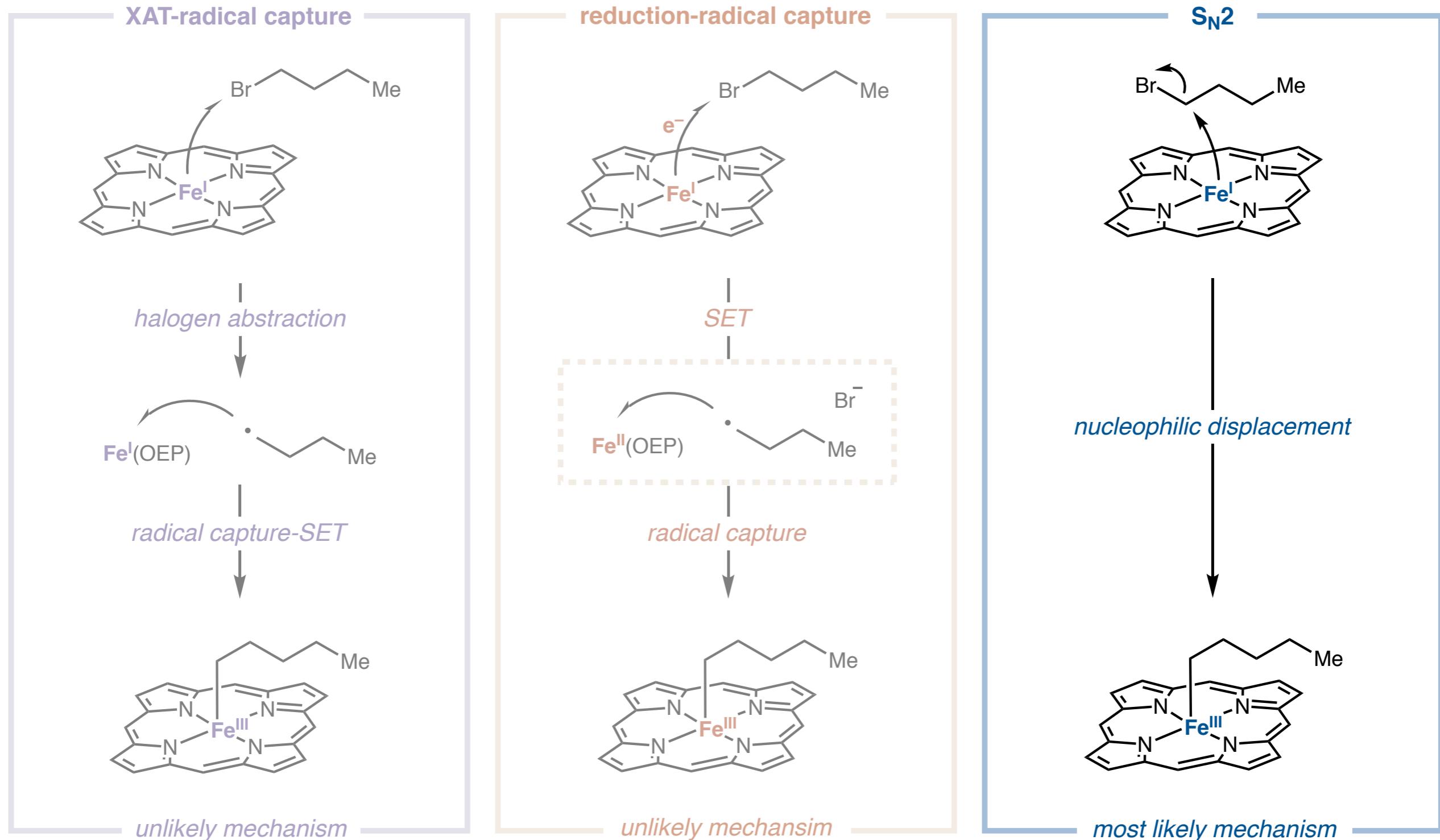


reduction potential of nucleophile

● = aromatic anion radicals

poor overlap with  
reactivity trends  
indicates  
direct reduction  
mechanism is unlikely

# Possible mechanisms of alkyl bromide activation by Fe(I) porphyrin



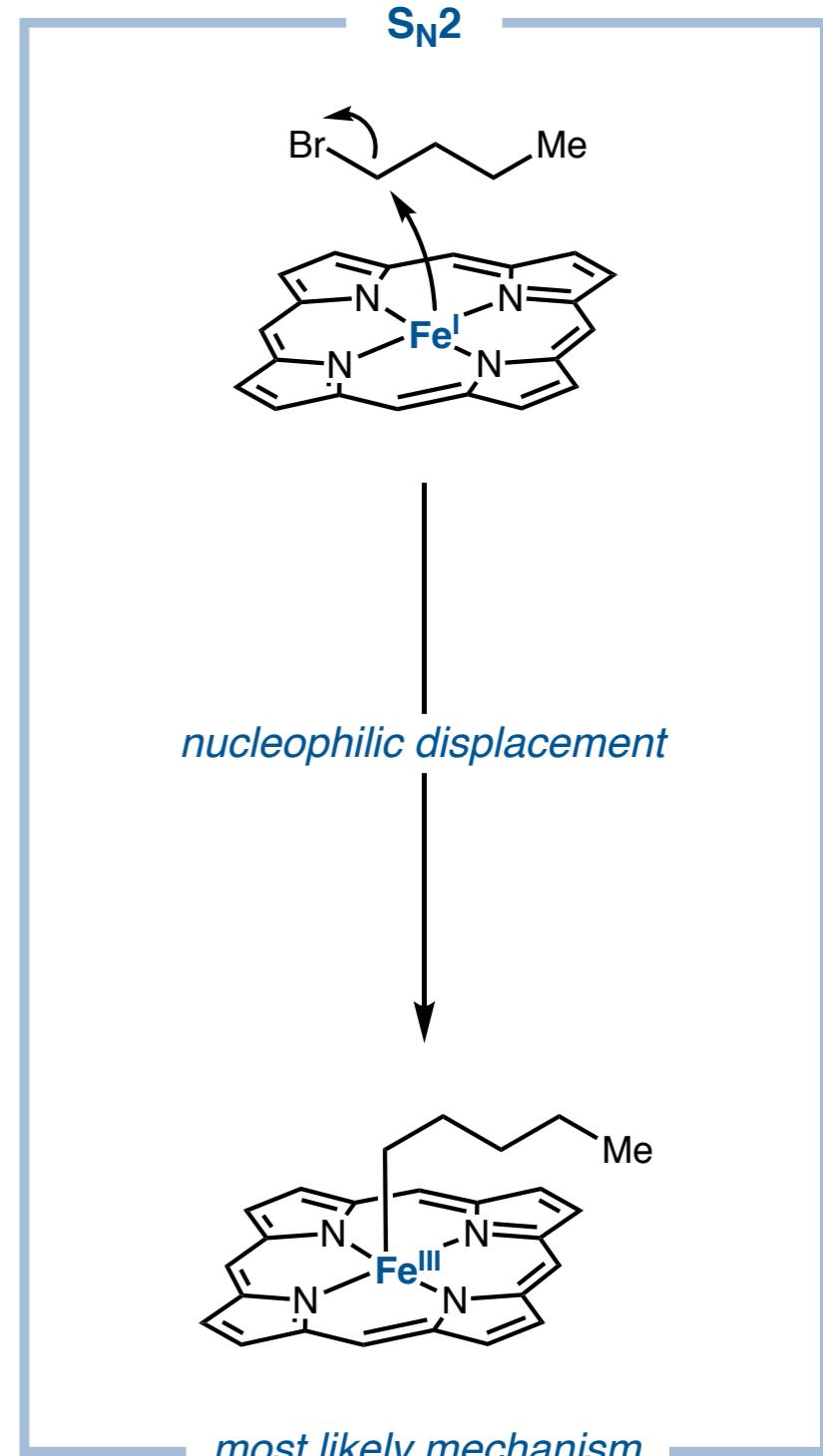
## Possible avenues of alkyl bromide activation by Fe(I) porphyrin

more electron-rich porphyrins yield more reactive metal centers:

**tetraphenylporphyrin < “hand basket” porphyrin < octaethylporphyrin**

more polarizable electrophiles react faster:

***n*-BuCl < *n*-BuBr < *n*-BuI**



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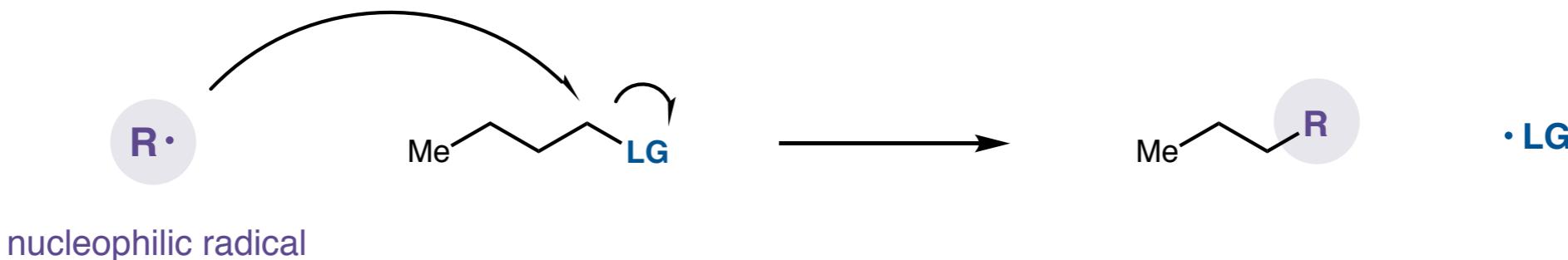
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# *The S<sub>H</sub>2 displacement mechanism*

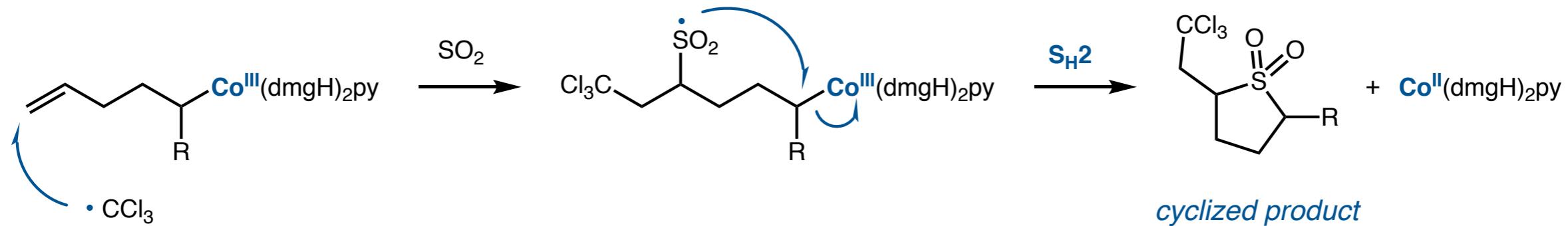
***“Seldom postulated, rarely discussed, frequently discarded as improbable,  
but potentially of immense interest in synthetic organic chemistry...”***

Bimolecular homolytic displacement of a radical from a saturated carbon by another radical  
*(the radical S<sub>N</sub>2)*

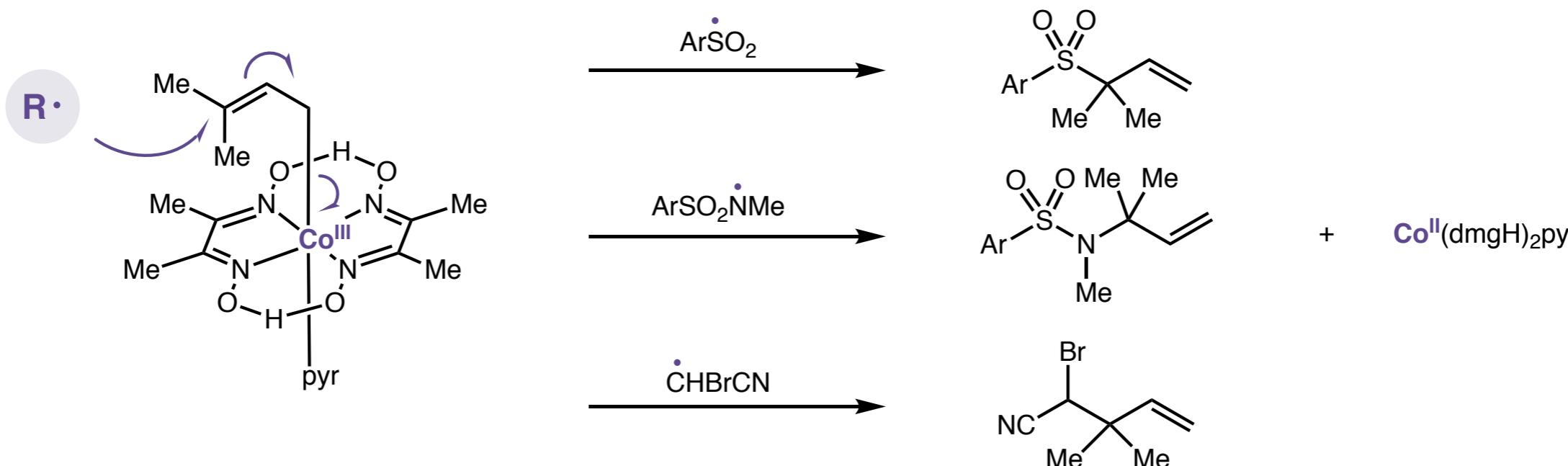


## *First row metal complexes as radical leaving groups*

*metal complexes have been shown to participate in  $S_{H}2$  mechanisms*



*intermolecular reactivity thoroughly exemplified for the  $S_{\text{H}}2'$  variant*



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*Questions?*

