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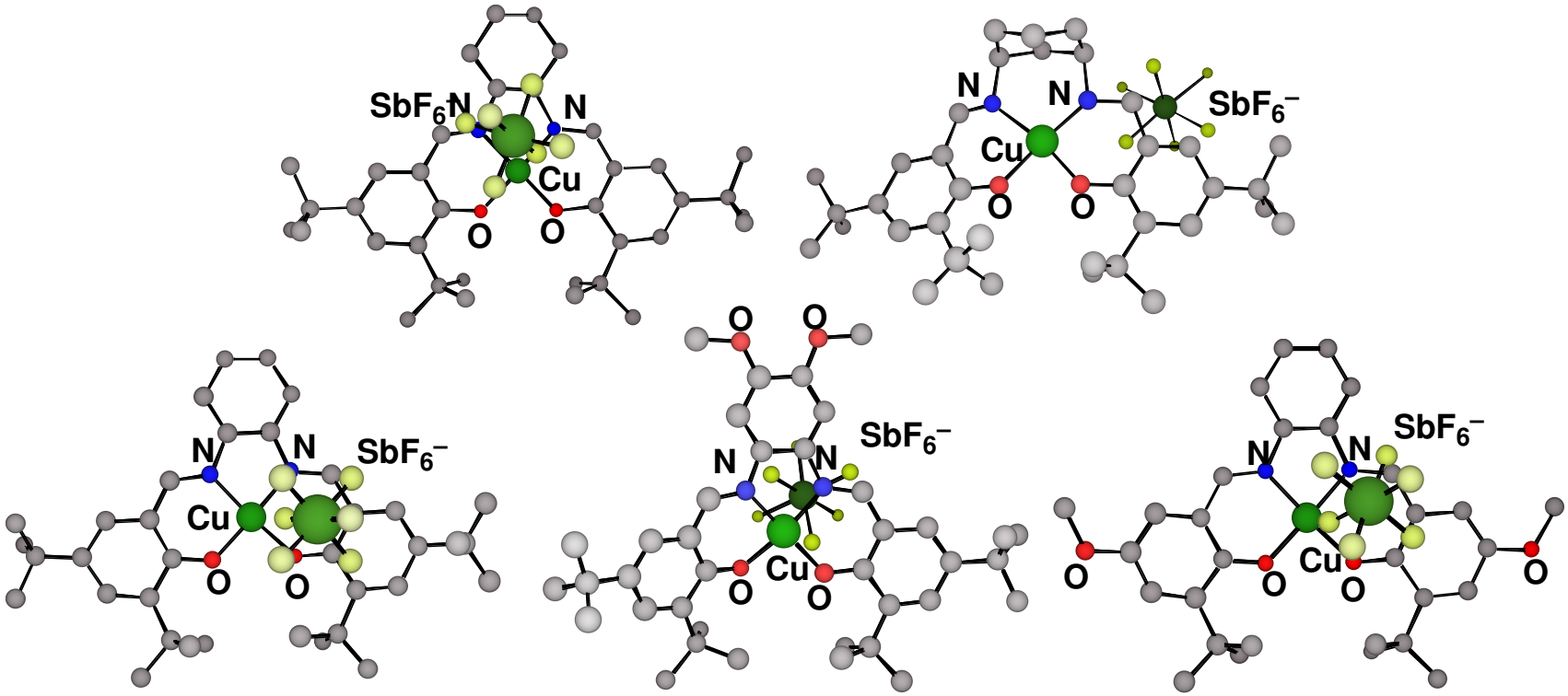
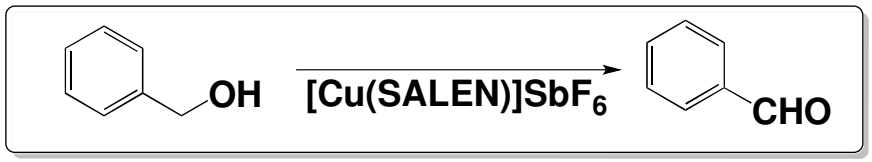
Oxidation Chemistry of Metal(II)-Diphenolato Complexes with Salen-Type Ligands; Electronic Structure and Reactivity Relationship





Yuichi Shimazaki

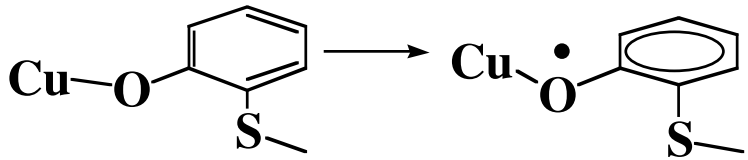
College of Science, Ibaraki University

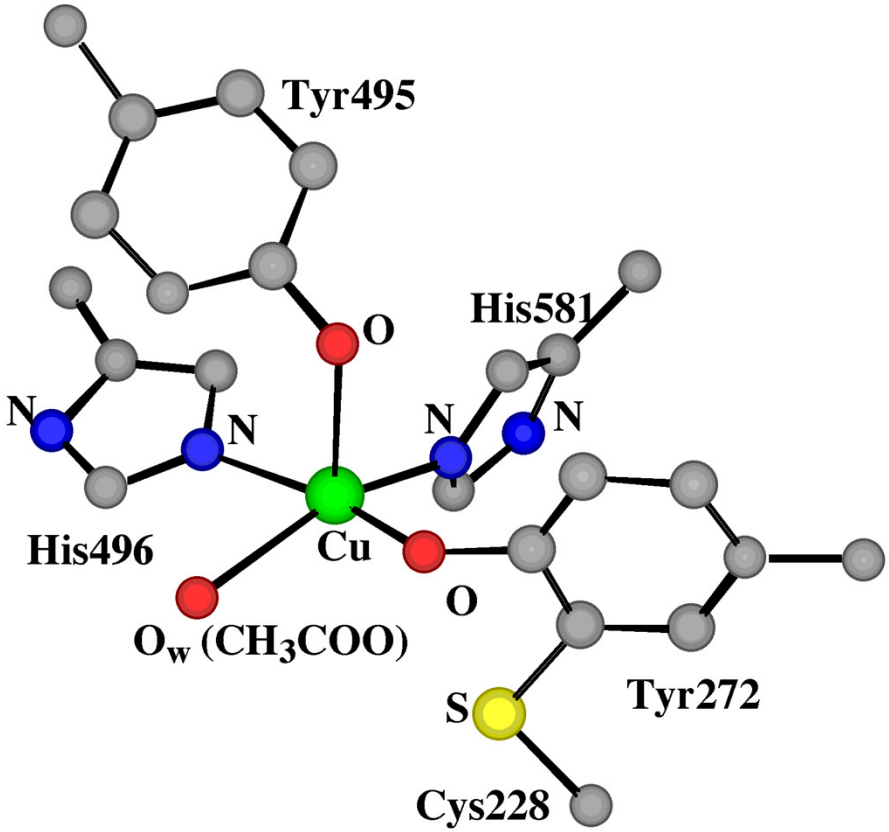
Galactose Oxidase (GOase)

- Cu ion
- Two-electron oxidant

RCH_2OH (primary alcohol) ⟶ RCHO (aldehyde)

- Two O(phenol) and two N(imidazole) donors
- Cu(II)-phenoxyl radical

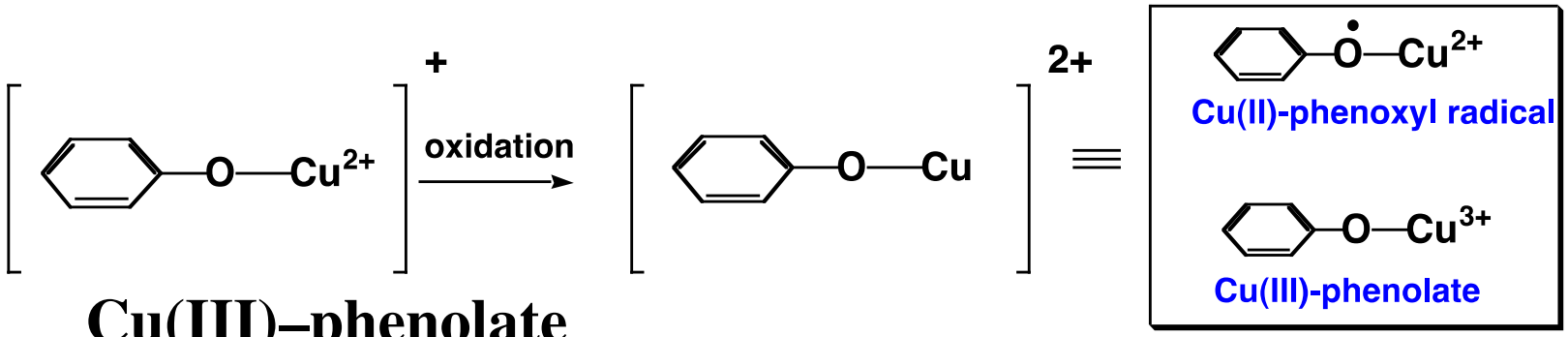




N. Ito, S. E. V. Phillips, K. D. S. Yadav, and P. F. Knowles, *J. Mol. Biol.*, *238*, 794(1994).

Cu(II)-phenoxyl radical vs. Cu(III)-phenolate

Why does GOase choose the Cu(II)-phenoxyl radical?



Cu(III)–phenolate

Metal-centered oxidation

d^8-configuration, diamagnetic species

The phenolate moiety should show phenolate characteristics

Cu(II)–phenoxyl radical

Phenolate-centered oxidation

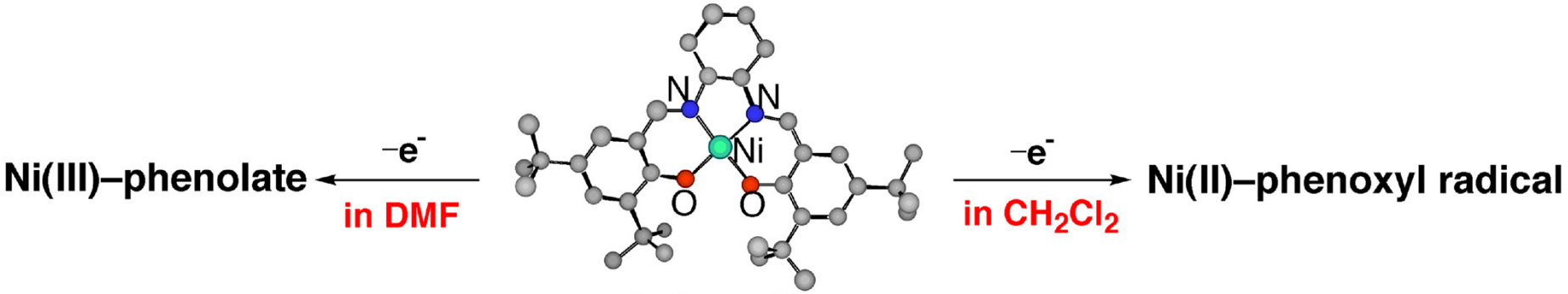
The Cu ion should have Cu(II) ion characteristics

Phenolate moiety should show the phenoxyl radical properties (but, different from the "free phenoxyl radical")

Magnetic exchange interaction between Cu and radical electrons.

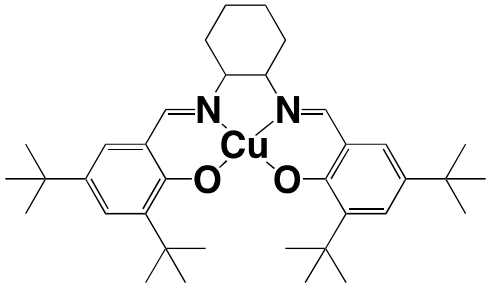
Relationship between the different valence state and the reactivity.

Y. Shimazaki, in *The Chemistry of Metal-Phenolates* (Ed. J. Zabicky), *John Wiley & Sons,* **2014**, pp 593-667.
Y. Shimazaki, in *Electrochemistry* (Ed. M. A. A. Khalid)、*InTech,* **2013**, pp 51-70.

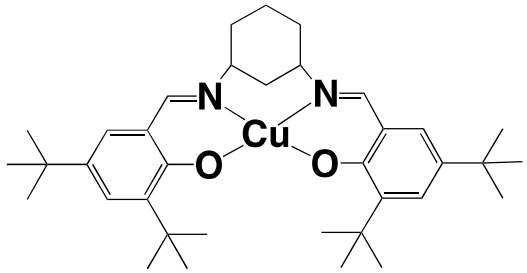


J. Am. Chem. Soc., **2003**, *125*. 10512.
J. Am. Chem. Soc., **2007**, *129*. 2559.
Inorg. Chem., **2009**, *48*. 8383.

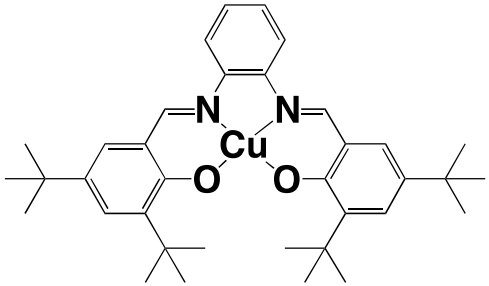
Small coordination environment changes may lead to the different valence state of the oxidized salen complex.



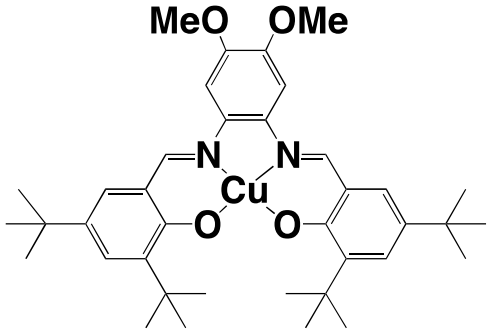
Cu(1,2-salcn)



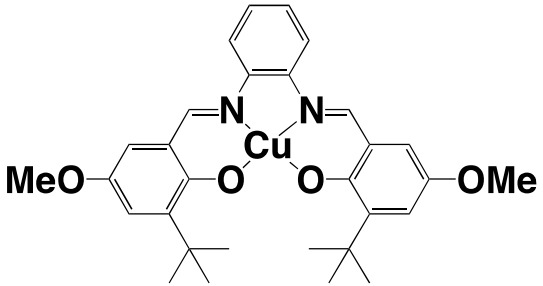
Cu(1,3-salcn)



Cu(salophen)



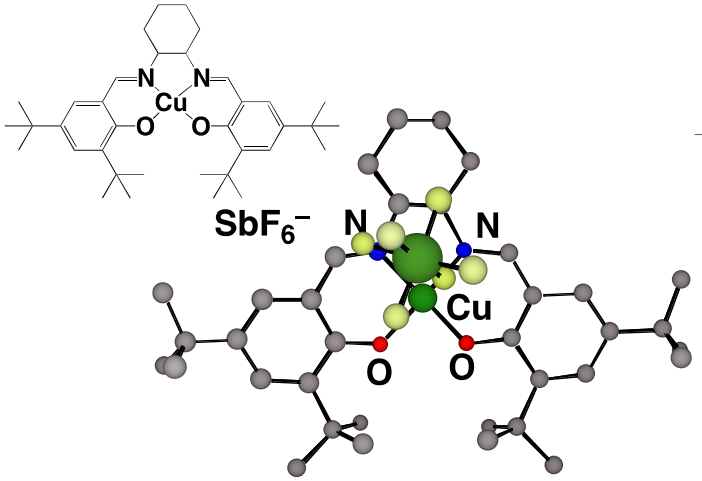
Cu(4,5-diMeOsalophen)



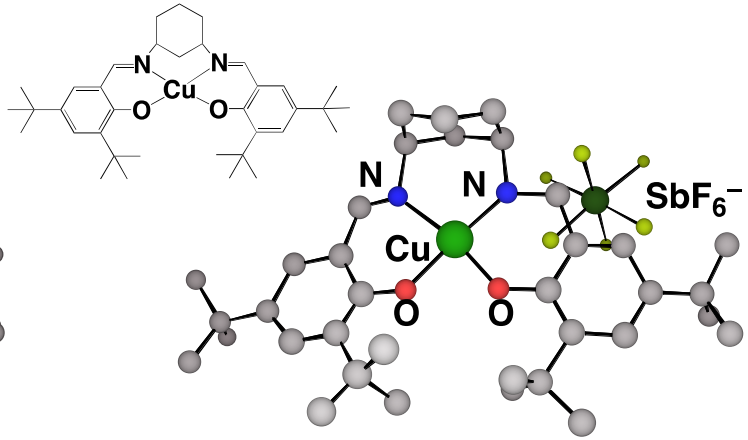
Cu(*p*-MeOsalophen)

cf. Chemistry & Biodiversity (Review), **2012**, *9*, 1635

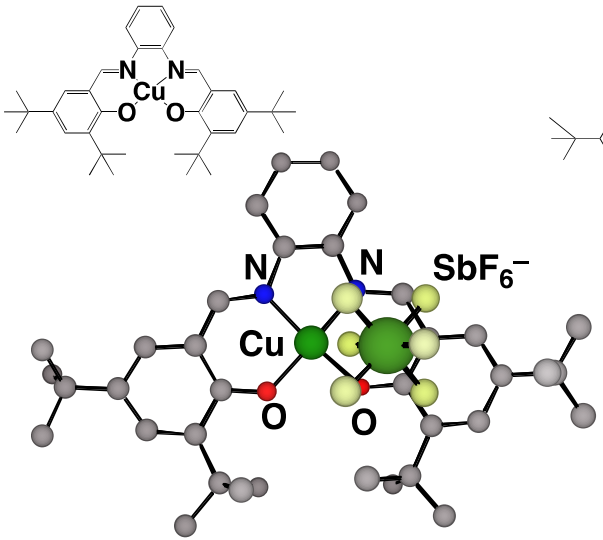
Summary of the electronic structures of oxidized SALENs



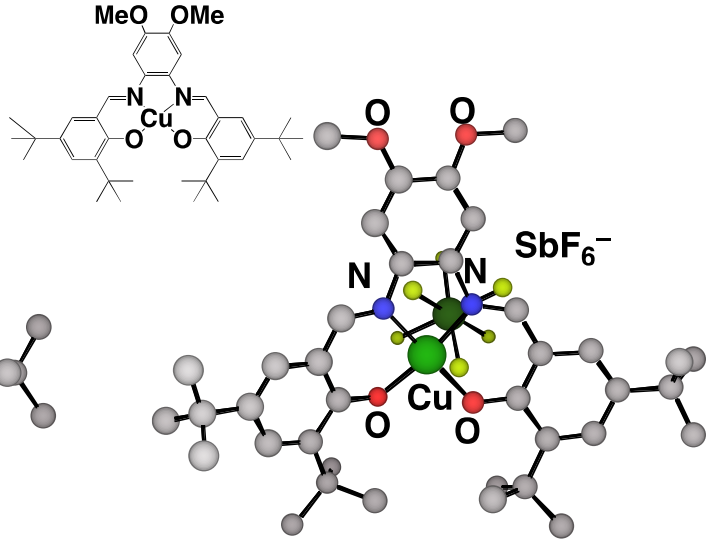
Equilibrium between Cu(III)-phenolate and Cu(II)-phenoxyl radical in CH_2Cl_2



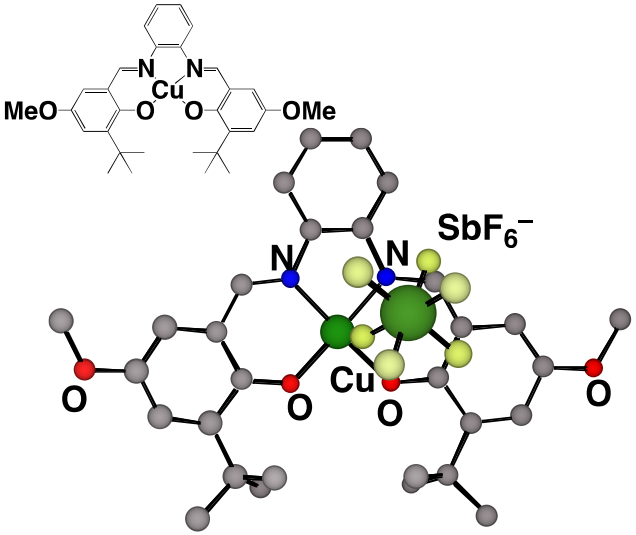
Cu(II)-relatively localized phenoxyl radical on the one-side of the phenolate



Cu(II)-phenoxyl radical at solid state while Cu(II)-ligand radical as a whole in CH_2Cl_2



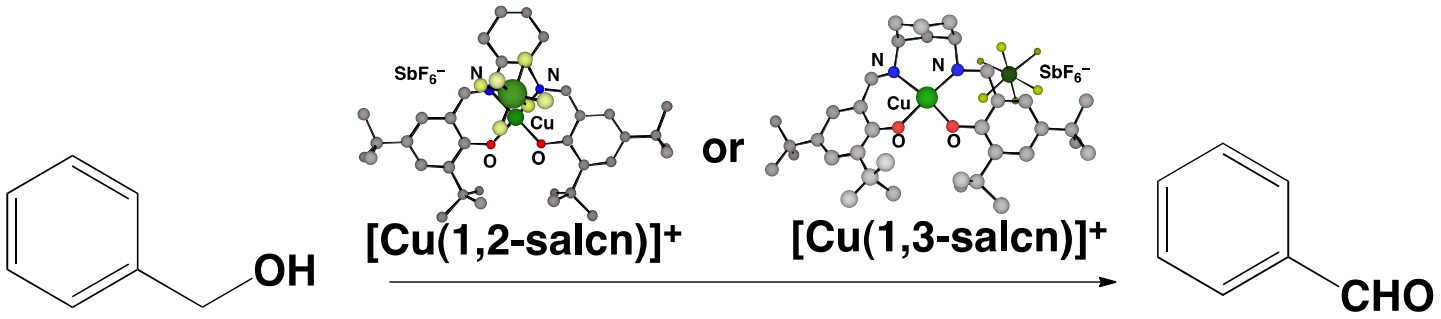
Cu(II)-*o*-diiminobenzen radical



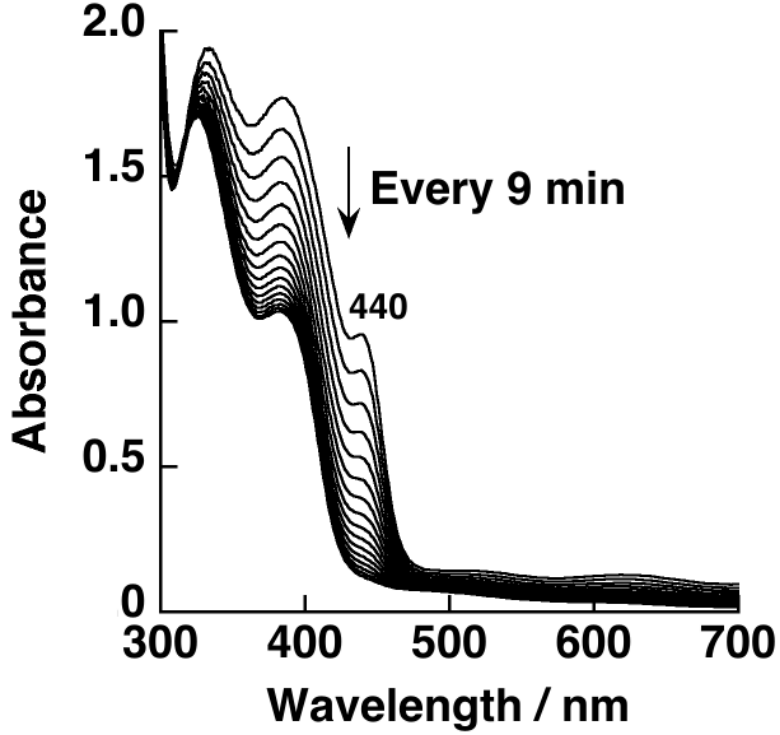
Cu(II)-relatively localized phenoxyl radical

J. Am. Chem. Soc., **2008**, *130,* 15448; *Chem. Eur. J.* **2012**, *18*, 1068; *Inorg. Chem.* **2012**, *51,* 12450; *Adv. Mater. Phys. Chem.*, **2013**, *3*, 60; *Dalton. Trans.* **2014**, *43*, 2283; *Pure and Appl. Chem.*, **2014**, *86*, 163.

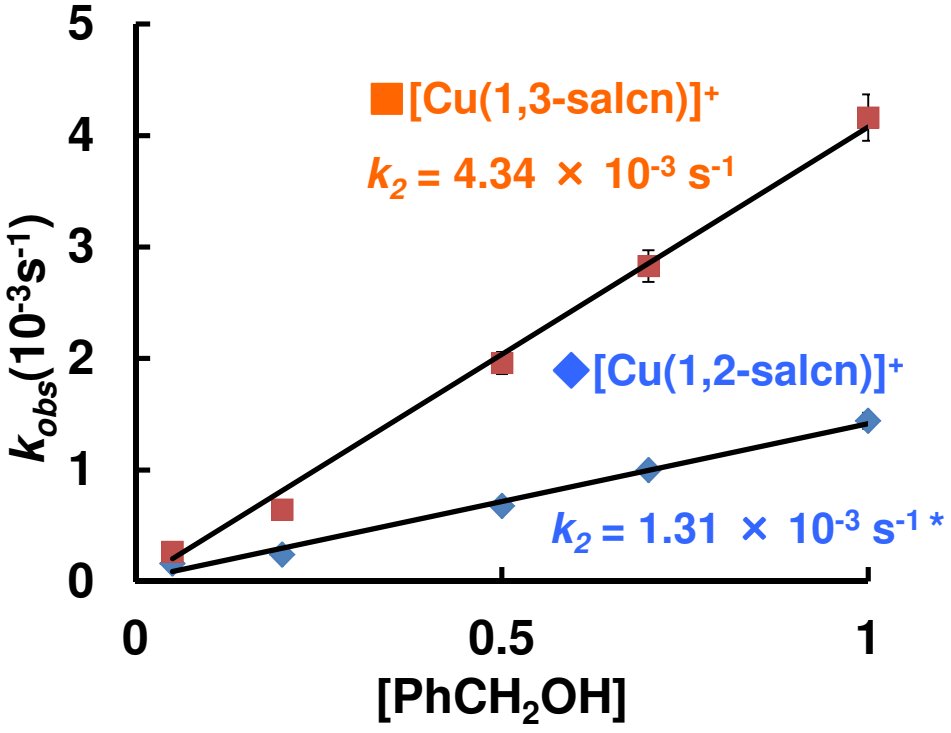
Reaction of [Cu(salcn)]⁺ with benzyl alcohol



Absorption spectral change of the reaction of [Cu(1,3-salcn)]+ with $PhCH_2OH$ (1.0 M)

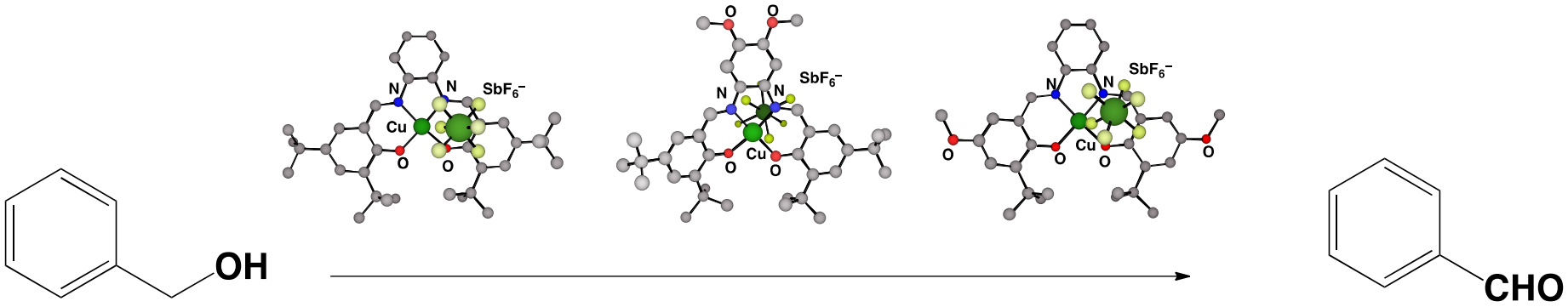


Reaction rate of oxidized Cu-salcns

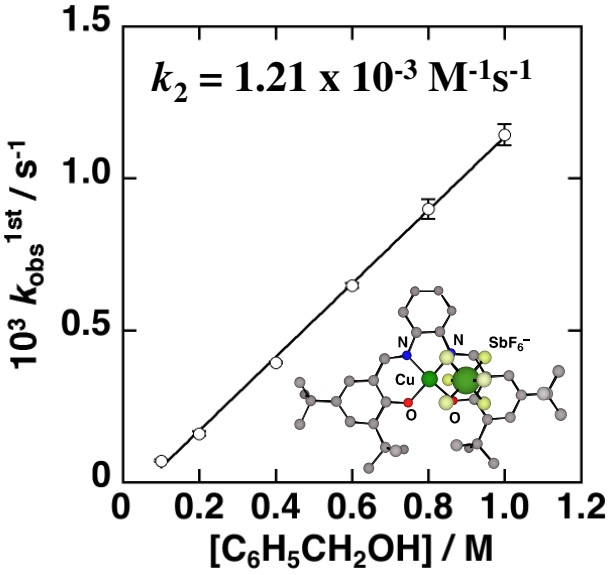


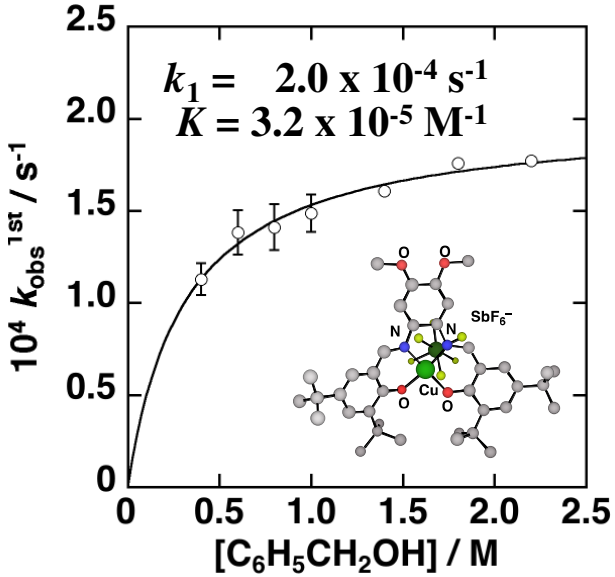
$$2[Cu(SALEN)]^+ + PhCH_2OH \longrightarrow 2Cu(SALEN) + PhCHO + H^+$$

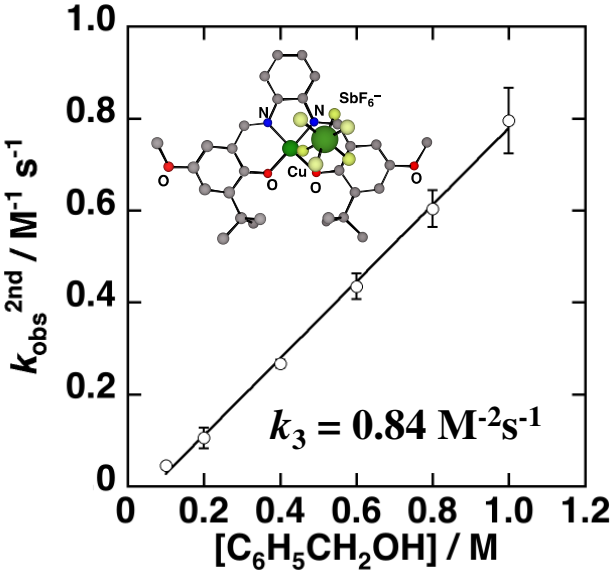
Reaction of [Cu(salophen)]$^+$ with benzyl alcohol



Reaction rate of oxidized Cu-salophens



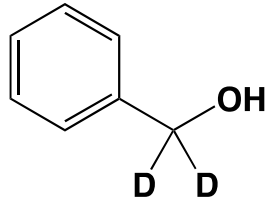




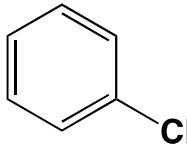
Different kinetics:

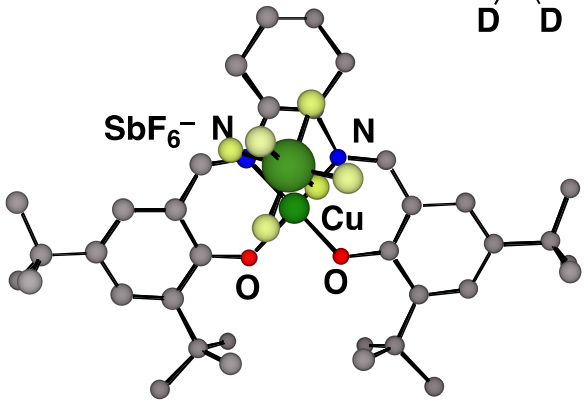
- **Without methoxy group (left); very similar to the salcn complexes**
- **Methoxy substituted *o*-phenylenediamine complex (middle); substrate saturation**
- **Methoxy substituted phenolate complex (right); second order kinetics**

Kinetic isotope effect (KIE)



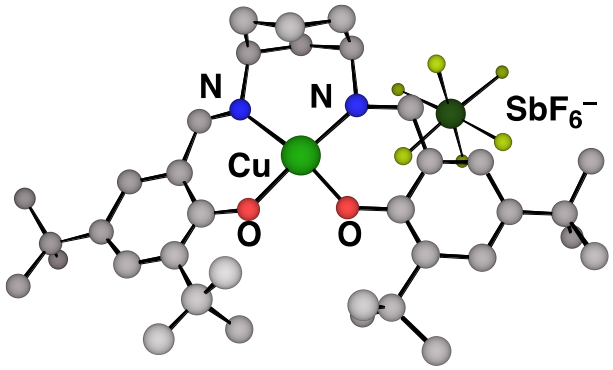
[Cu(SALEN)]$^+$





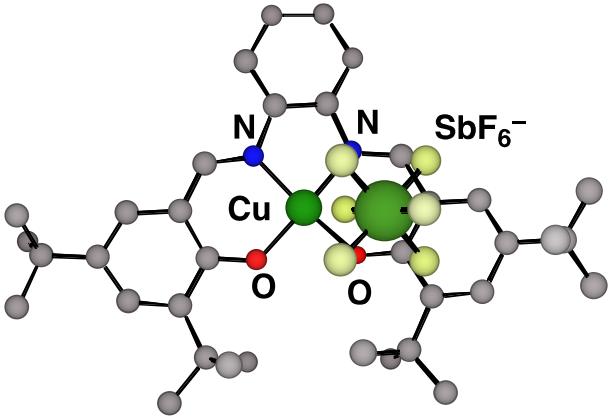
Equilibrium between Cu(III)-phenolate and Cu(II)-phenoxyl radical

KIE = 19



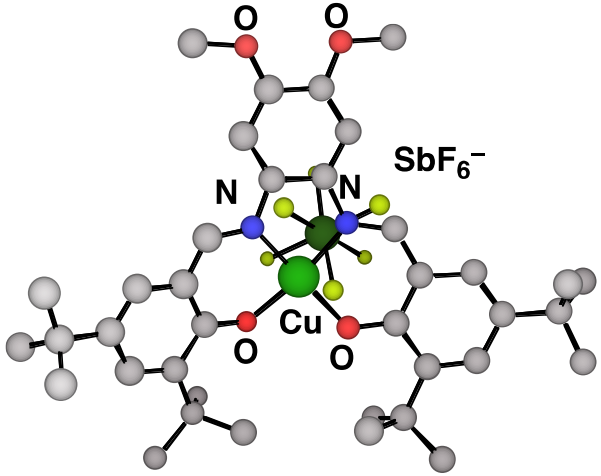
Cu(II)-relatively localized phenoxyl radical on the one-side of the phenolate

KIE = 13



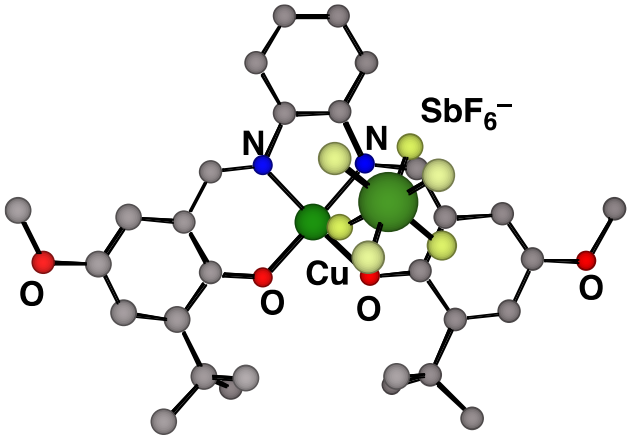
Cu(II)-ligand radical as a whole

KIE = 13



Cu(II)-*o*-diiminobenzene radical

KIE = 1.5

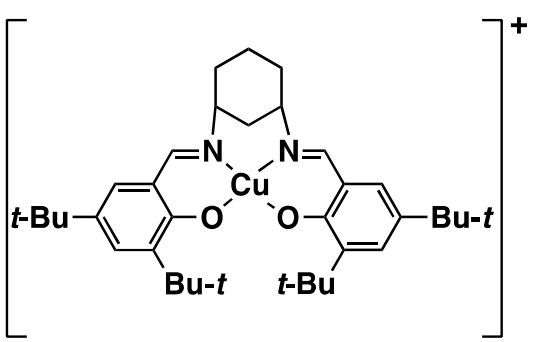


Cu(II)-relatively localized phenoxyl radical on the one-side of the phenolate

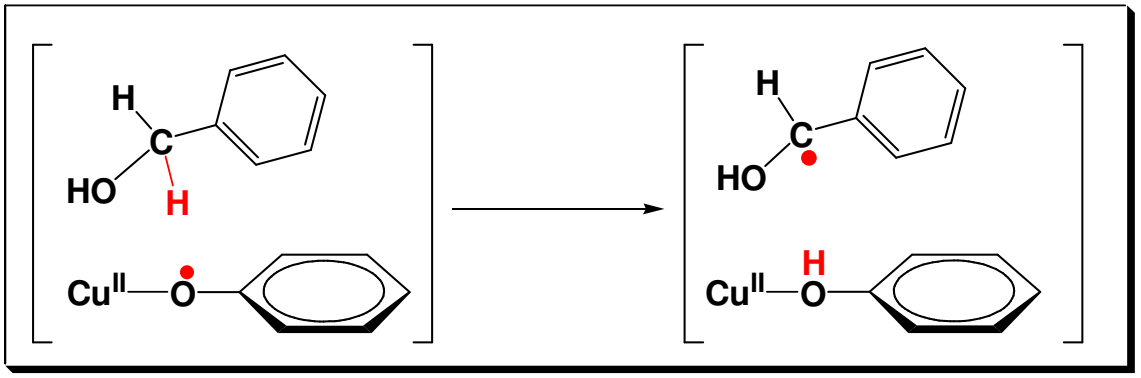
KIE = 1.0

Reaction mechanisms

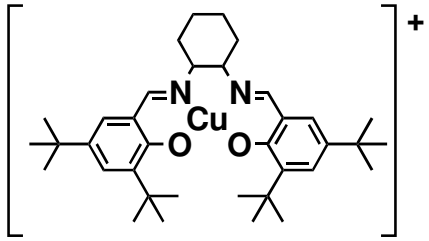
○ Hydrogen abstraction mechanism for Cu(II)-phenoxyl radical



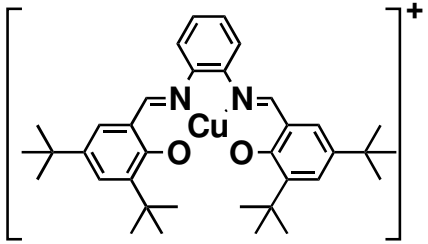
Cu(II)-phenoxyl radical



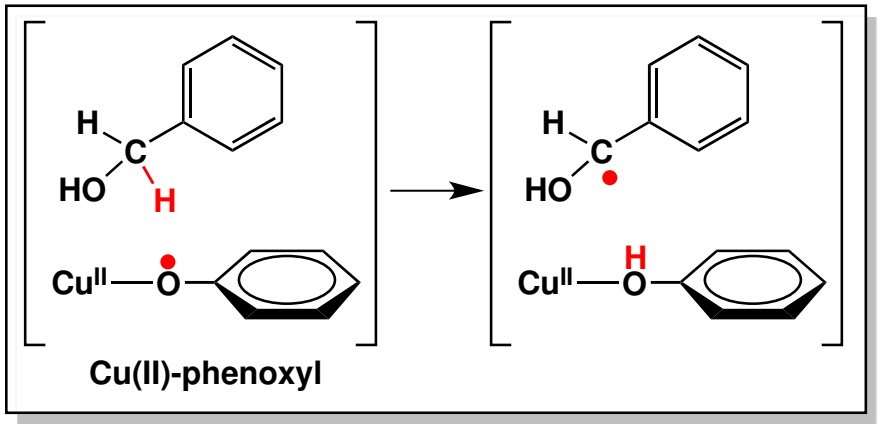
○ Hydrogen abstraction of Cu(III)-phenolate or Cu(II)-ligand radical is unfavorable in comparison to the Cu(II)-phenoxyl radical



Cu(III)-phenolate



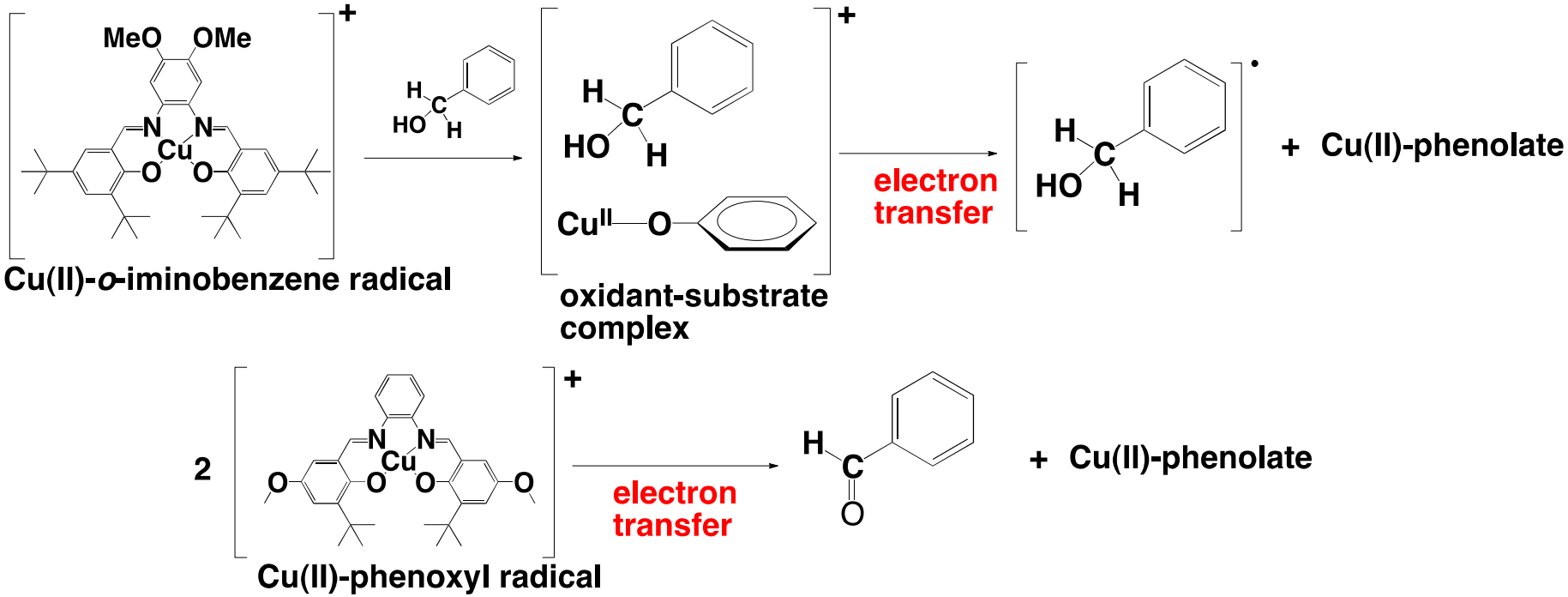
Cu(II)-ligand radical



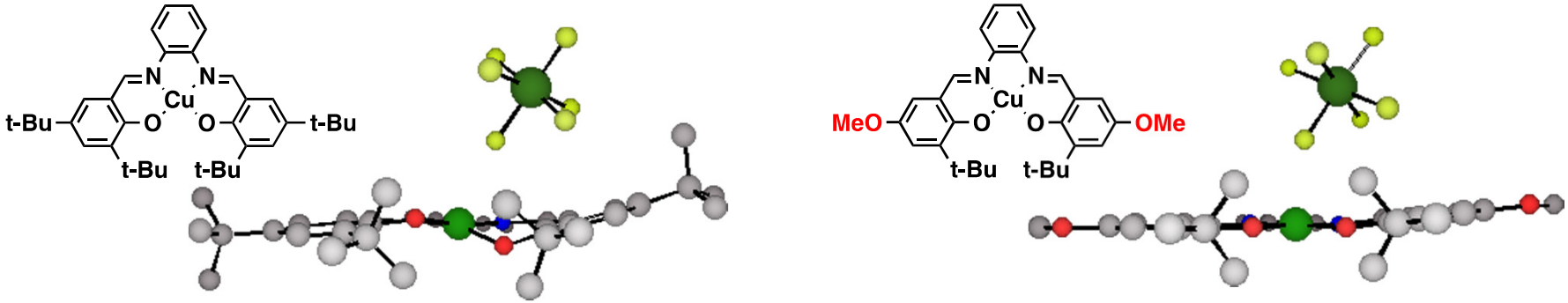
Inorg. Chem. **2012**, *51*, 12450; *Dalton Trans.*, **2014**, *43*, 2283; *Pure and Appl. Chem.*, **2014**, *86*, 163.

Hydrogen abstraction vs. Electron transfer

○ Methoxy substituted complexes are electron transfer mechanism.



flexibility of the phenoxyl radical may be important.



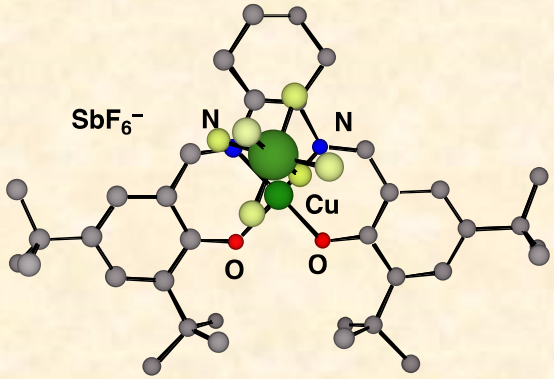
Hydrogen abstraction

Electron transfer

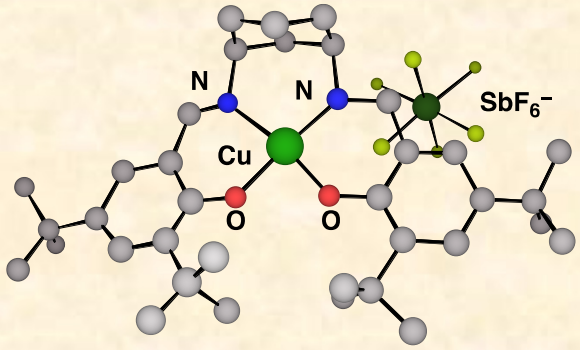
Dalton Trans., **2014**, *43*, 2283.

— *Summary* —

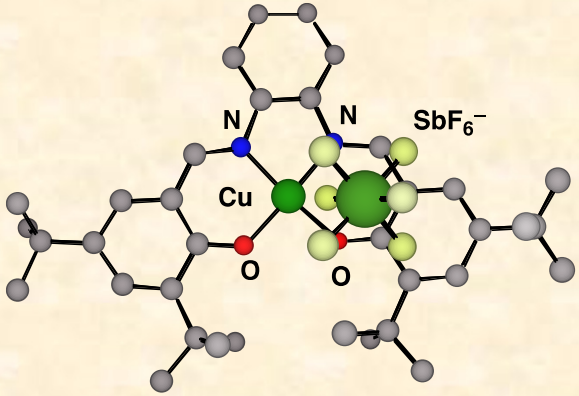
Characterization of the one-electron oxidized Cu(II)-salen complexes



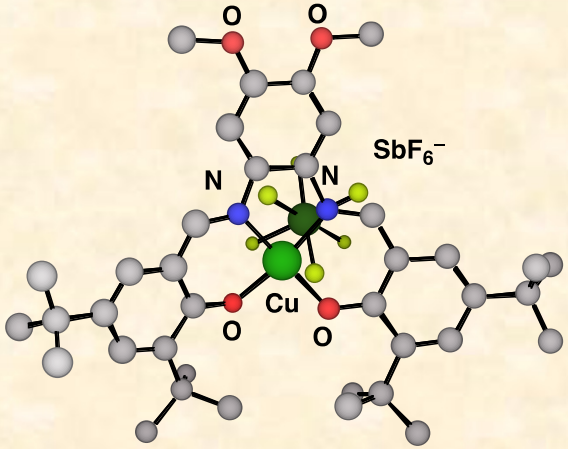
Equilibrium between Cu(III)-phenolate and Cu(II)-phenoxyl radical in CH_2Cl_2



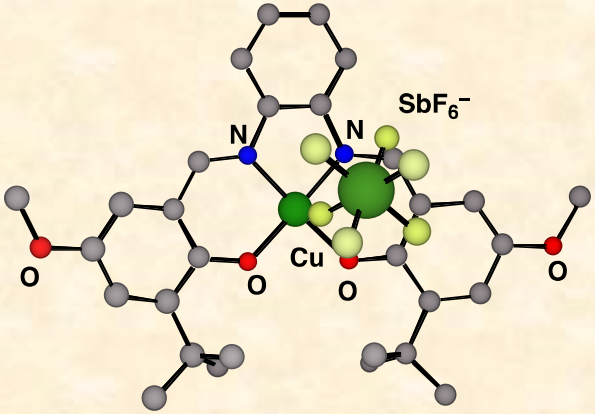
Cu(II)-relatively localized phenoxyl radical on the one-side of the phenolate



Cu(II)-ligand radical as a whole in CH_2Cl_2



Cu(II)-*o*-diiminobenzen radical



Cu(II)-relatively localized phenoxyl radical

Reactivity of the oxidized Cu(II)-salcn complexes

- Reaction mechanism depends on the electronic structures of oxidized complexes
- Hydrogen abstraction of flexible phenoxyl radical complex is more favorable.
- Rigid radical species are less reactive for benzyl alcohol oxidation.

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