Utilizing fluorinated copper(I) scorpionate complexes for ethylene chemistry and their catalytic applications

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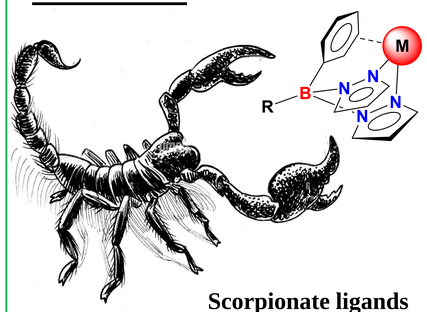
Introduction:

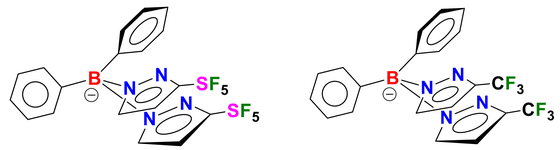


Scorpionate ligands

Scorpionate ligands are a class of polydentate ligands that strongly coordinate to metal centers, resembling a scorpion's grasp. They have found extensive use in transition metal and organometallic chemistry due to their stability, tunability, and ability to modulate electronic and steric properties of metal complexes. Their applications span catalysis, bioinorganic chemistry, and materials science.

Motivation:

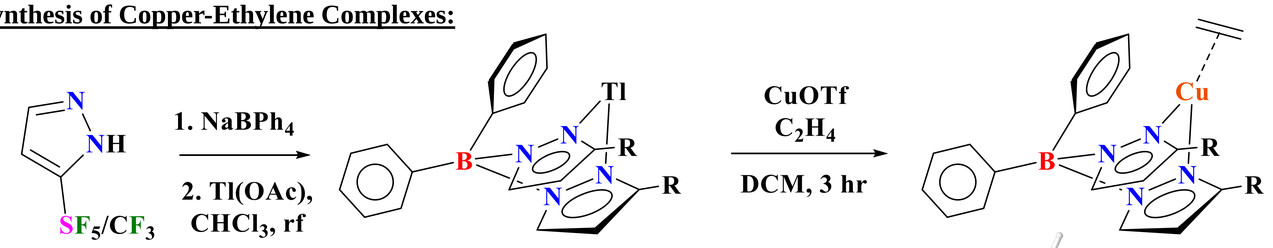
- Utilize the use of two fluorinated bis(pyrazolyl)borate ligands.



- Studying effect of electron-withdrawing groups SF_5 vs. CF_3 of copper-ethylene complexes.
- Comparison of their copper-ethylene complexes for carbene and nitrene transfer chemistry.

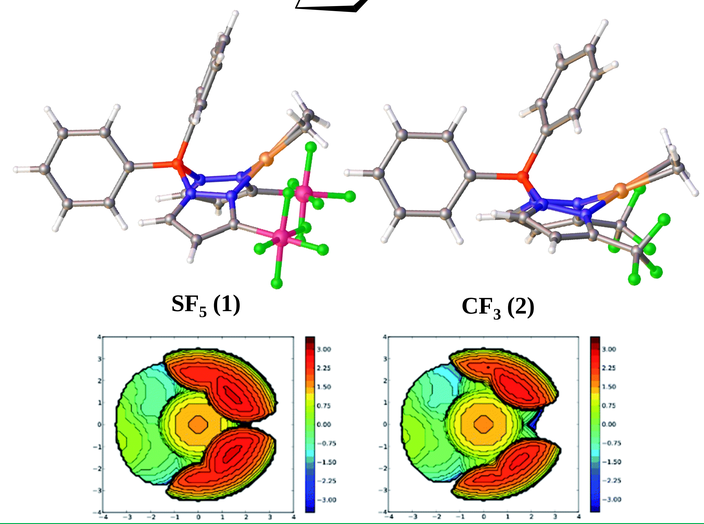
Trofimenko. S. *Chemical Reviews.* **1993**, *93(3)*, 943– 980.

Synthesis of Copper-Ethylene Complexes:



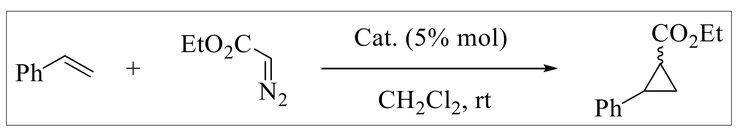
Compounds	^{1}H NMR (ppm)	Δ(^{1}H) (ppm)	^{13}C NMR (ppm)	Δ(^{13}C) (ppm)	% buried volume
Free C_2H_4	5.40	-	123.1	-	-
SF_5 (1)	3.72	-1.68	86.4	-36.7	69.9
CF_3 (2)	3.69	-1.71	82.7	-40.4	64.0

The SF_5 ligand is a weaker donor and more sterically demanding than the CF_3 ligand



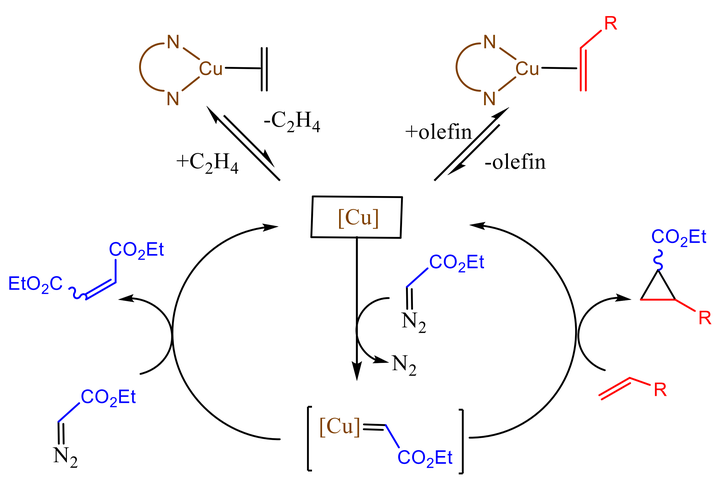
Noonikara-Poyil. A *et al. Chemical Science.* **2021**, *12(43)*, 14618– 14623.

Catalytic activity on carbene transfer chemistry:



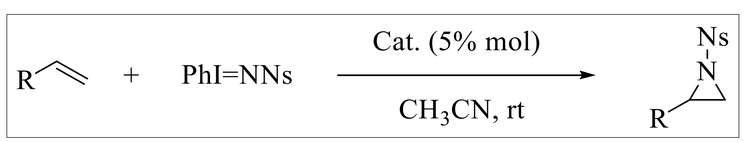
Catalyst	Yield	Cis/Trans
SF_5 (1)	99%	61/39
CF_3 (2)	62%	48/52

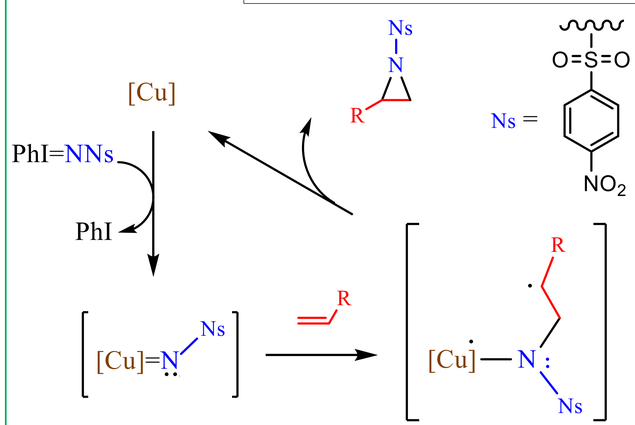
- Yield in cyclopropanation is related to the use of electron deficient ligands.
- Higher *cis*-selectivities associated with bulkier supporting ligands



Diaz-Requejo, M.M *et al. J. Am. Chem. Soc.* **2002**, *124(6)*, 978– 983.

Catalytic activity on Nitrene transfer chemistry:





Catalyst	R = Ph	R = *n*-Bu	R = *t*-Bu
SF_5 (1)	99%	71	63
CF_3 (2)	99%	65	60

- The reaction is triggered by the formation of a metal–nitrene intermediate in the triplet state

Maestre. L *et al. J. Am. Chem. Soc.* **2013**, *135(4)*, 1338– 1348.

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