

Tailor-Made Ligands for Transition Metal Catalysis



Forschungskolloquium der Chemischen Institute

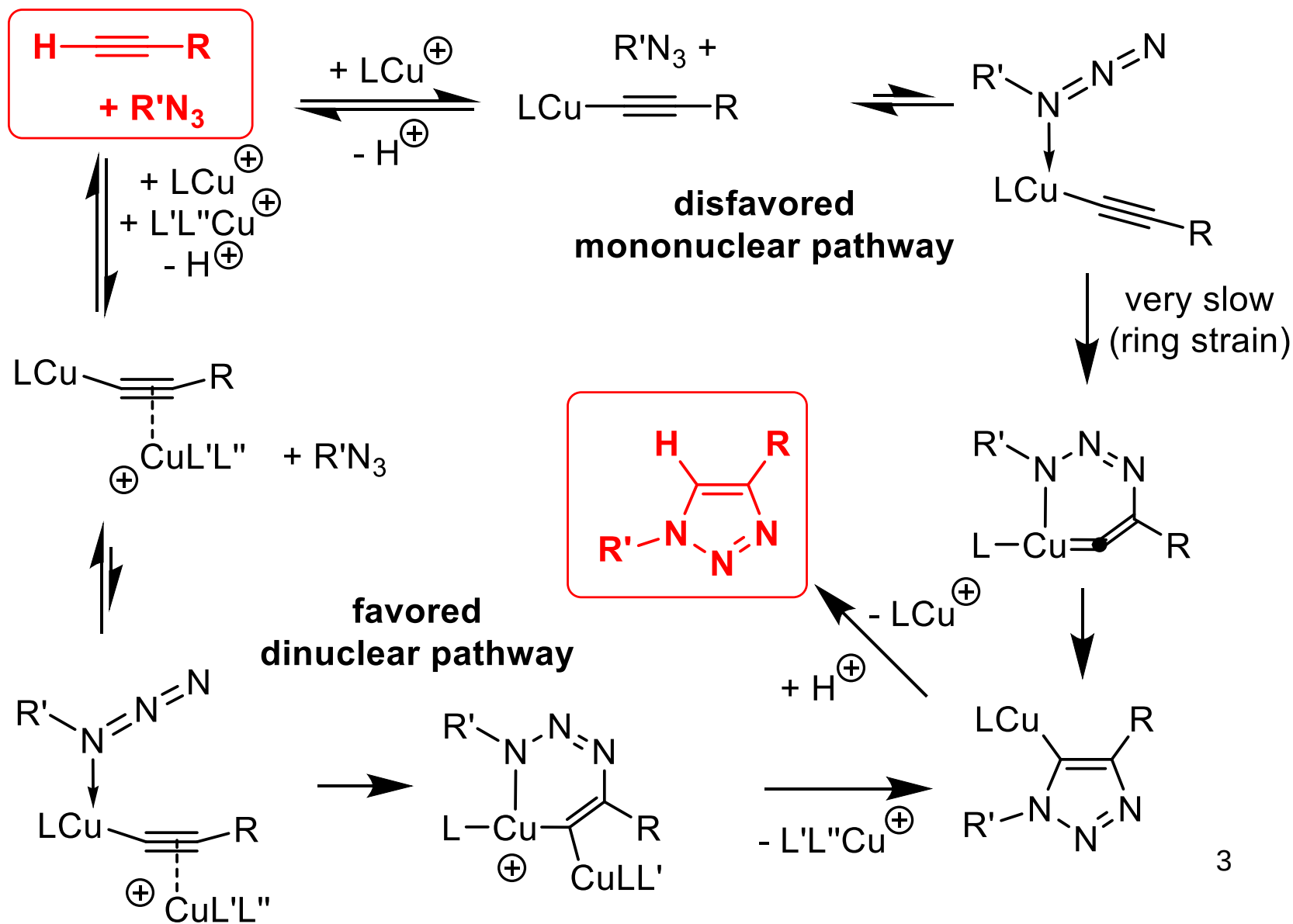
14.12.2017

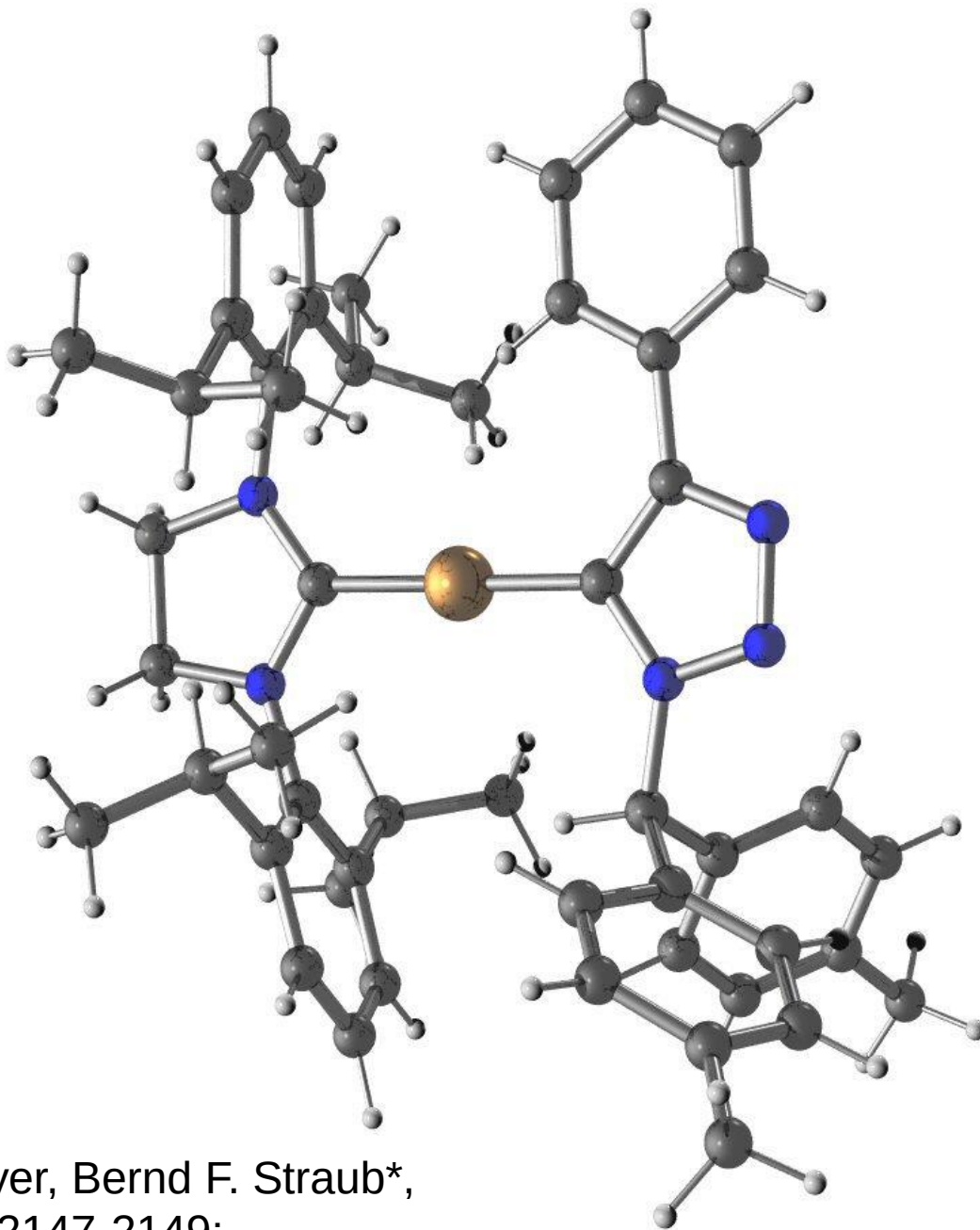
Prof. Dr. Bernd F. Straub

Organisch-Chemisches Institut, Universität Heidelberg

Bridging N-Heterocyclic Carbene Ligands for CuAAC Catalysis

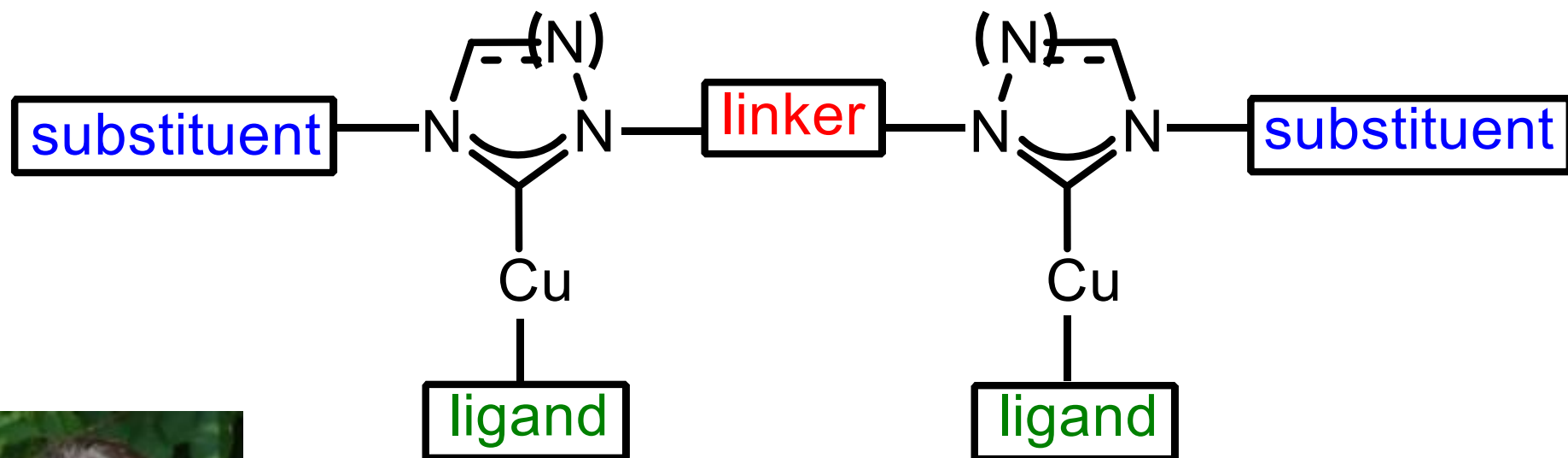
CuAAC Mechanism





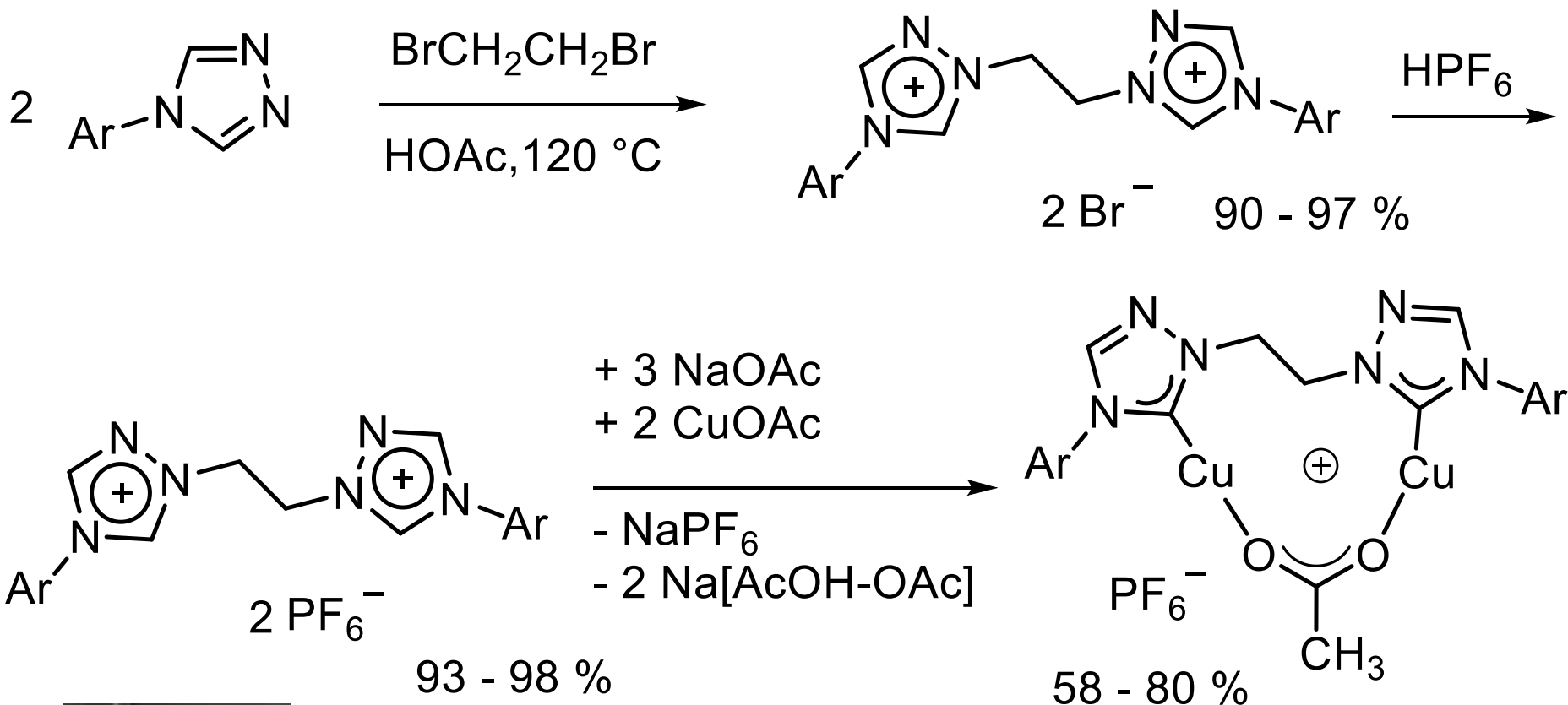
Christoph Nolte, Peter Mayer, Bernd F. Straub*,
Angew. Chem. **2007**, *119*, 2147-2149;
Angew. Chem. Int. Ed. **2007**, *46*, 2101-2103

Catalyst Design: Irreversible Coordination of Two Copper(I)



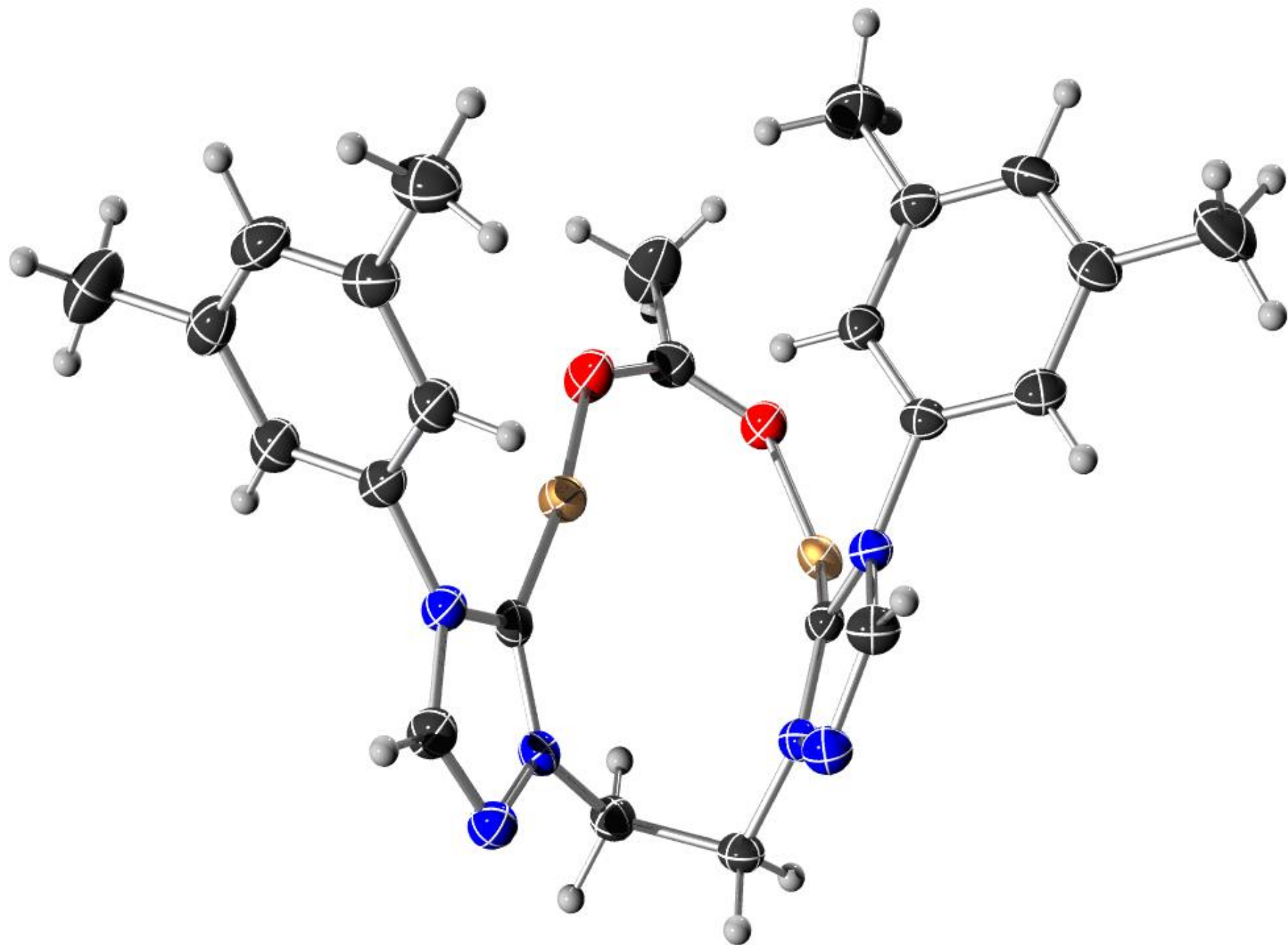
Review: Regina Berg,* Bernd F. Straub*,
Beilstein J. Org. Chem. **2013**, 9, 2715-2750.

Acetate as Sacrificial Ligand

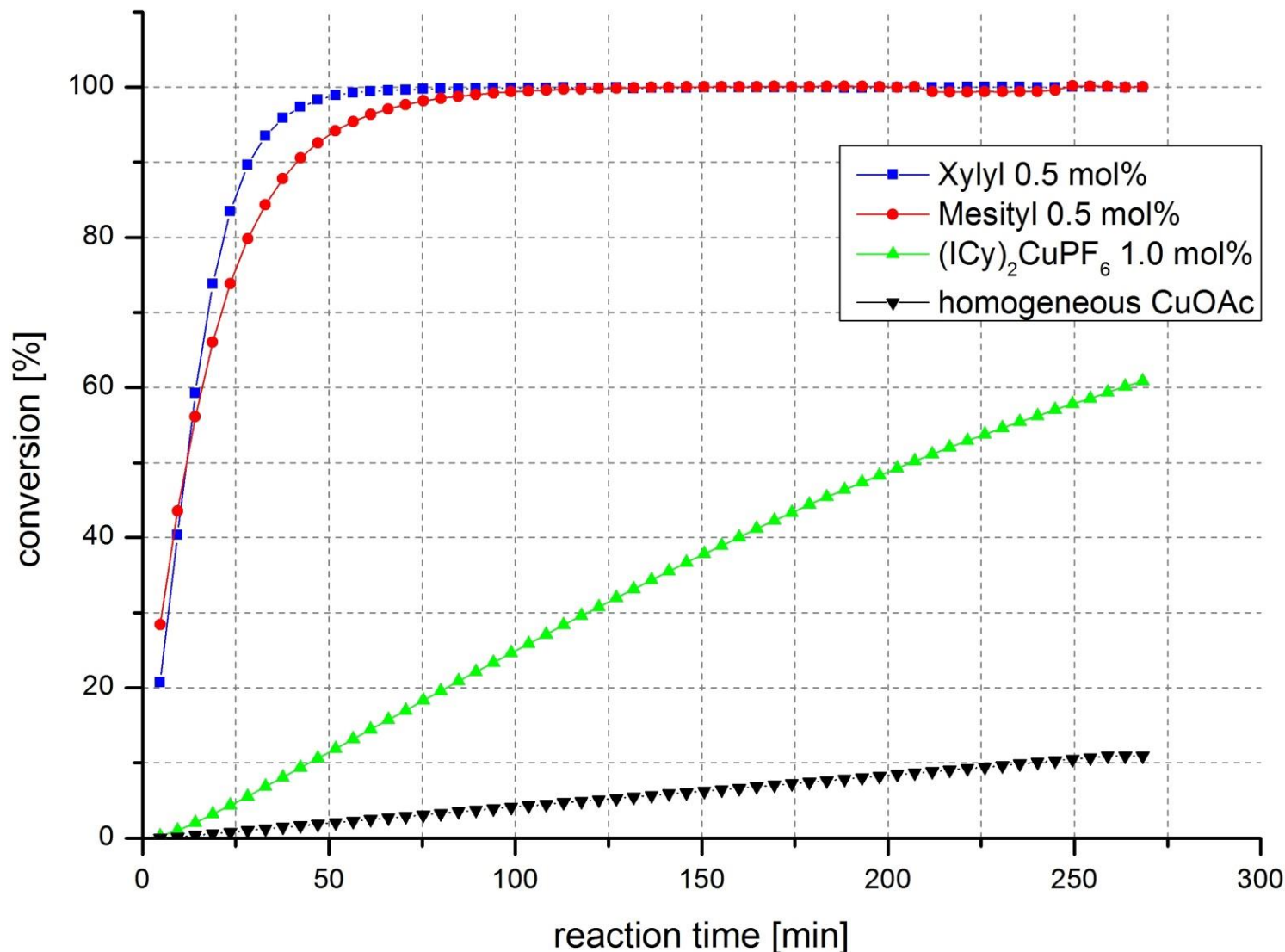


Regina Berg, Johannes Straub, Ella Schreiner,
 Steffen Mader, Frank Rominger, Bernd F. Straub*,
Adv. Synth. Catal. **2012**, 354, 3445-3450.



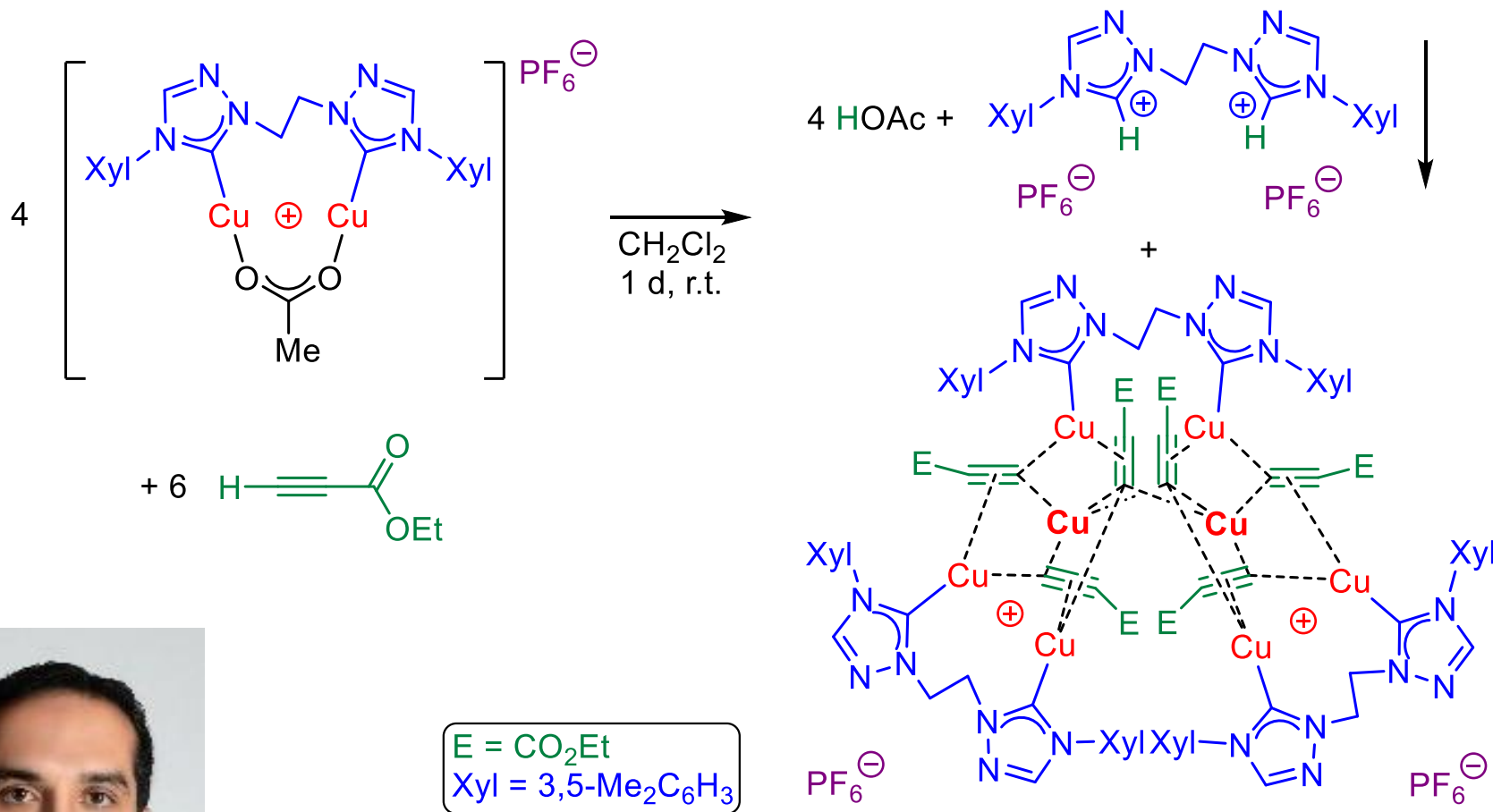


Homogeneous CuAAC Catalysis

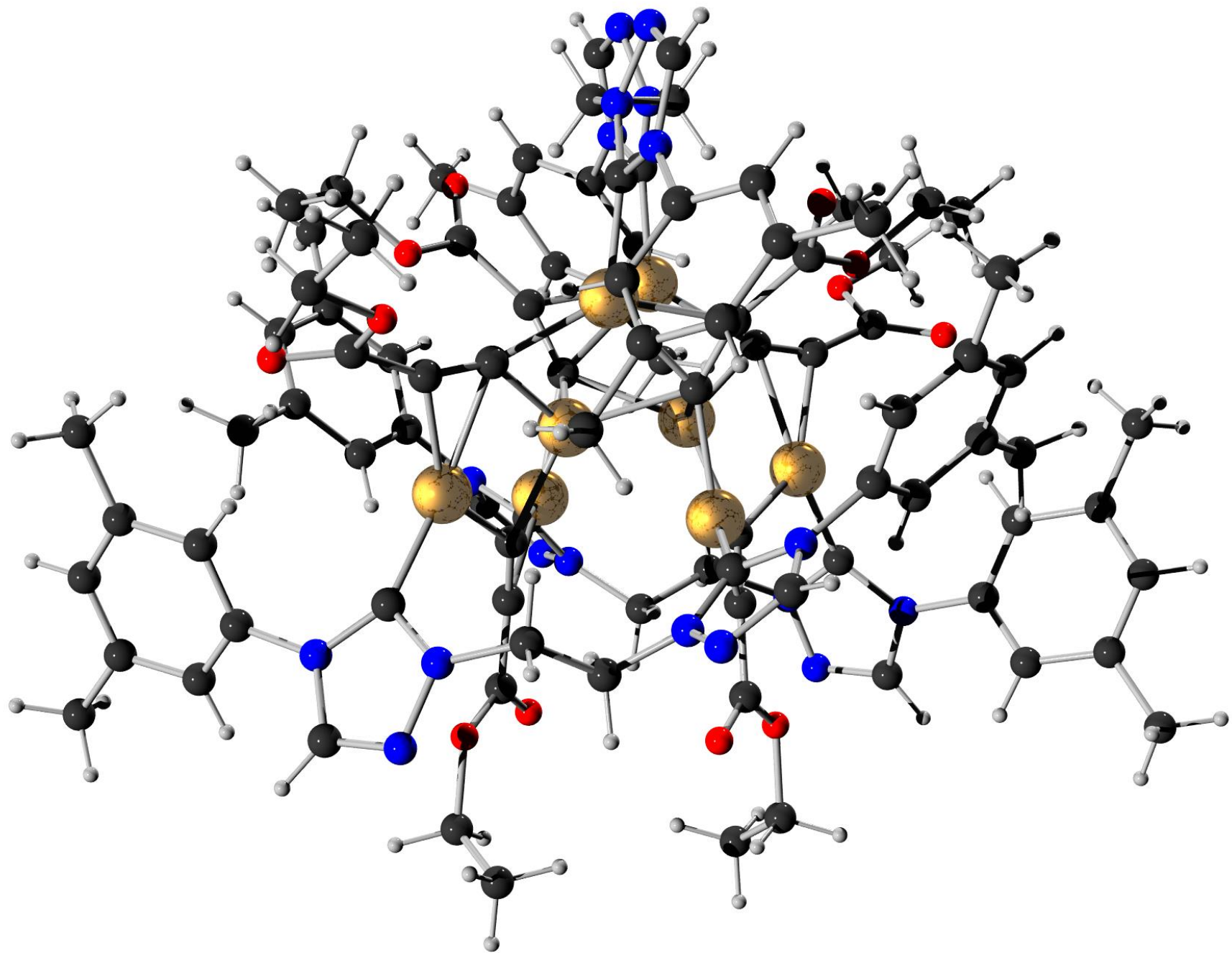


296 K,
CD₂Cl₂
0.6 M PhCCH
0.6 M BnN₃

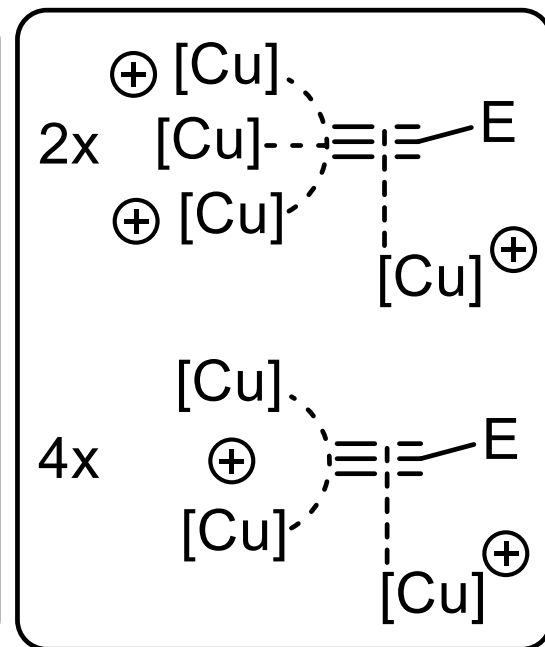
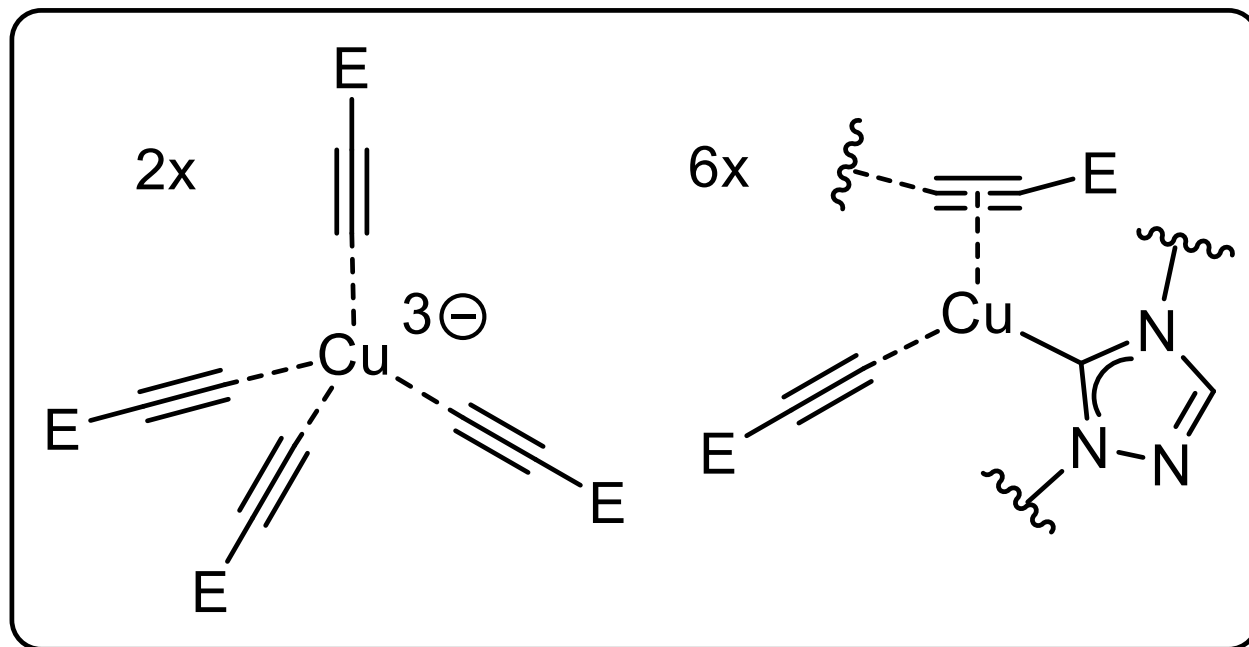
Formation of a Copper(I) Acetylide Cluster



Ata Makarem, Regina Berg, Frank Rominger, Bernd F. Straub*,
Angew. Chem. **2015**, 127, 7539-7543;
Angew. Chem. Int. Ed. **2015**, 54, 7431-7435.



Copper and Acetylide Coordination Modes



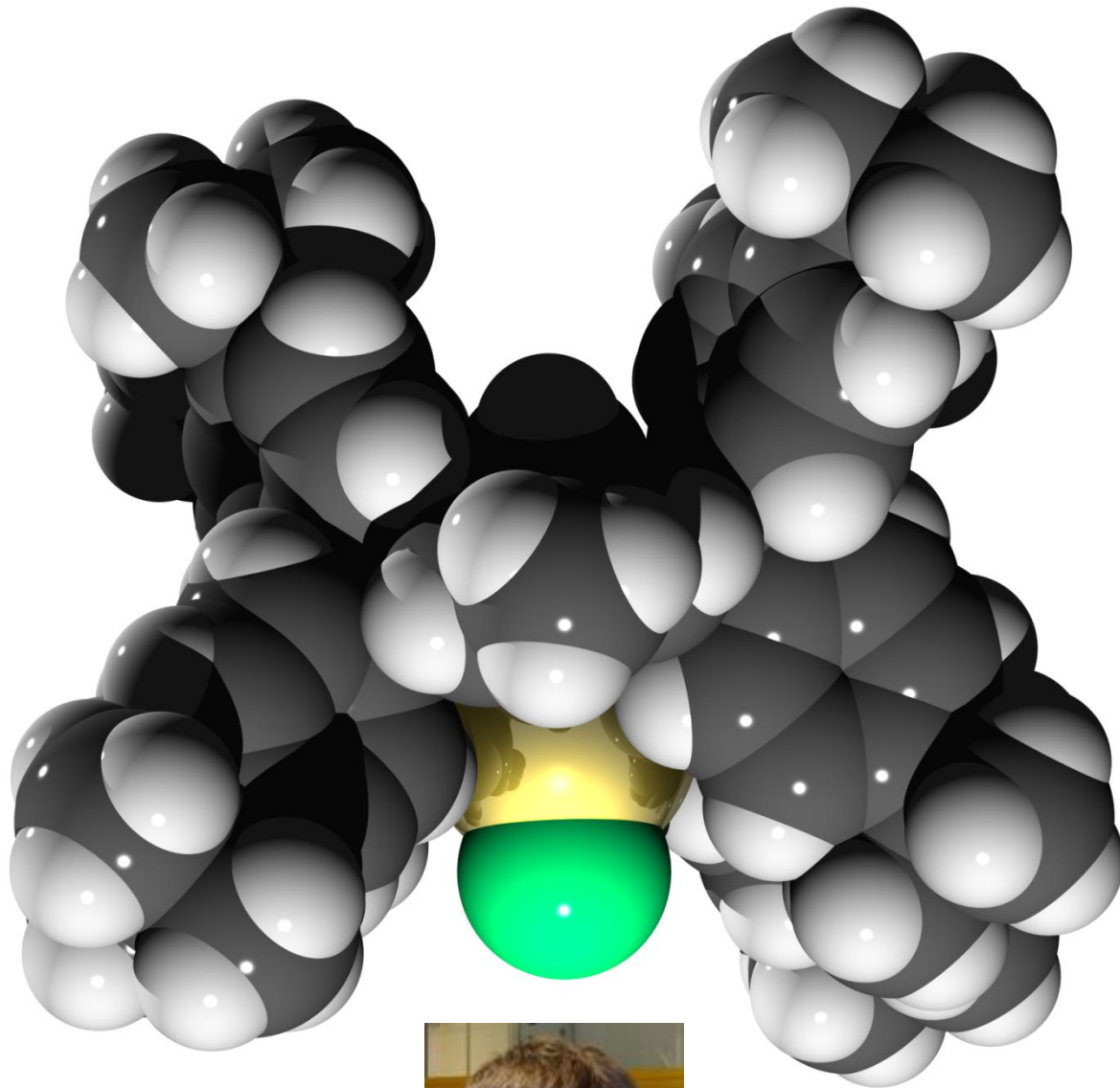
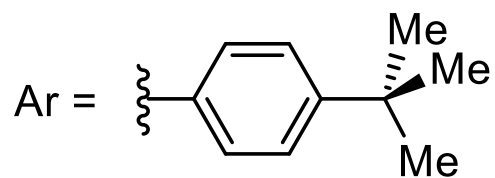
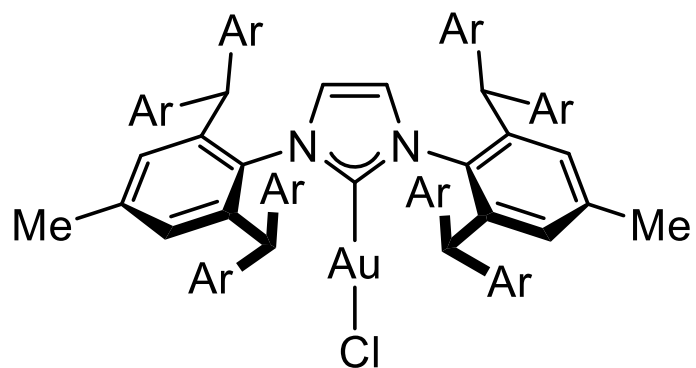
Goals

- Use of the modular principle of azol, linker, copper salt, base, and counterion
- Facile synthesis of catalytically highly active, air-stable, and water-soluble dicopper complex



Anne Schöffler, Ata Makarem, Frank Rominger, Bernd F. Straub*, *Beilstein J. Org. Chem.* **2016**, 12, 1566-1572.

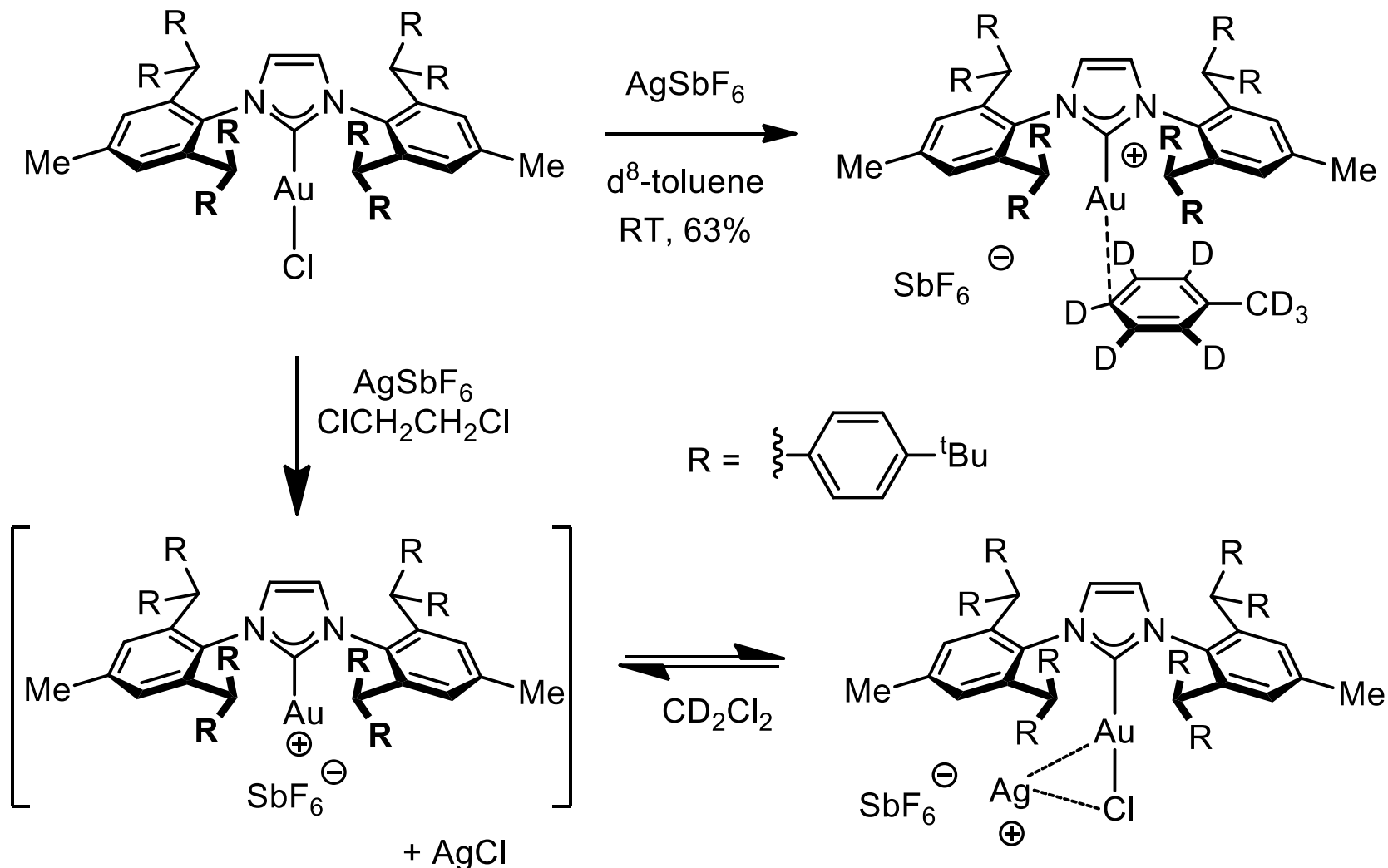
Sterically Shielded Ligand for True Gold Carbenes



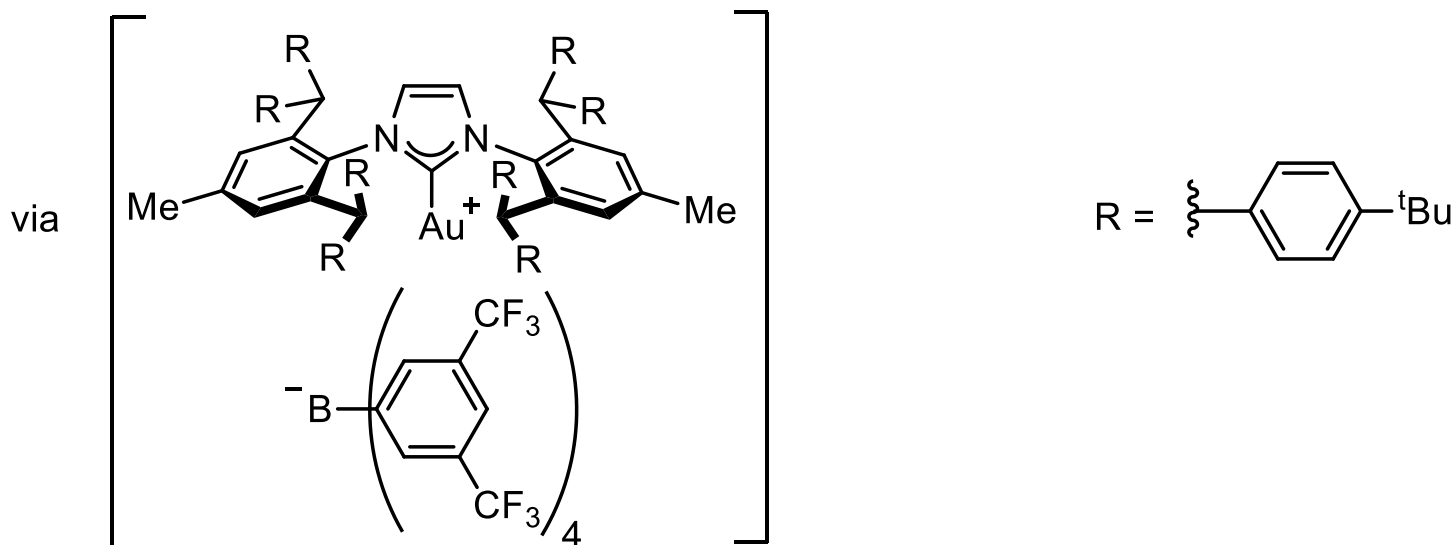
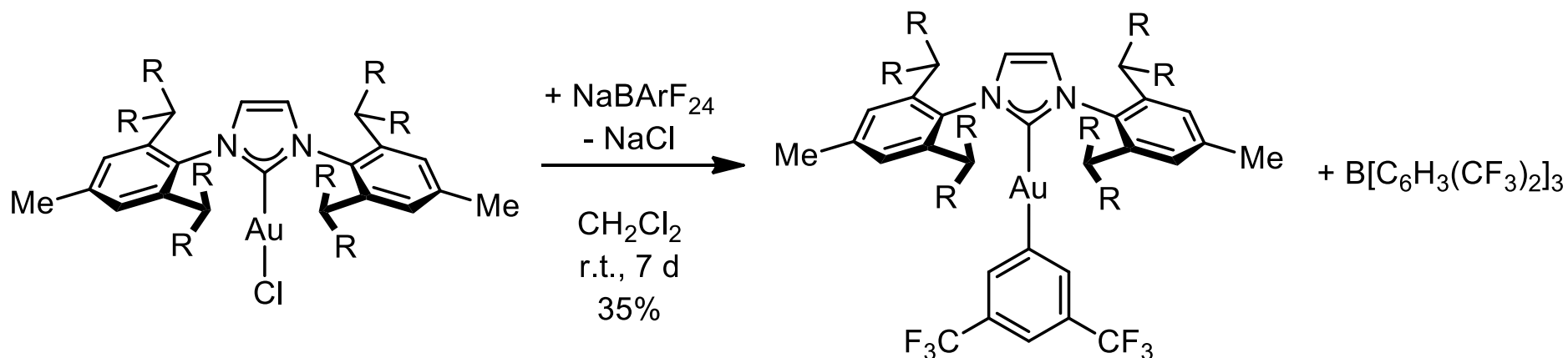
Simone G. Weber, Christian Loos,
Frank Rominger, Bernd F. Straub*,
ARKIVOC **2012**, 2, 226-242.

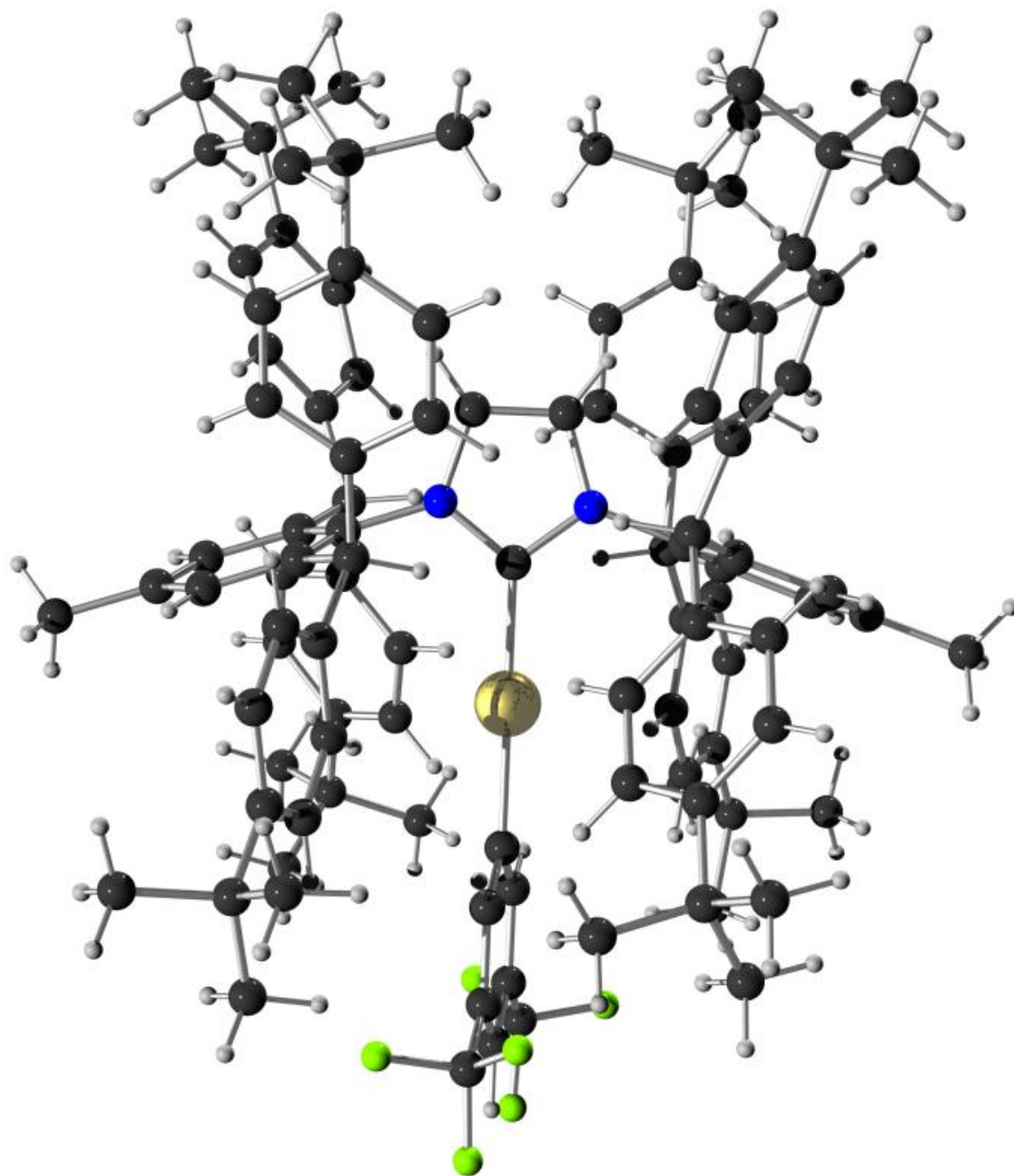


Silver Caught Red-Handed

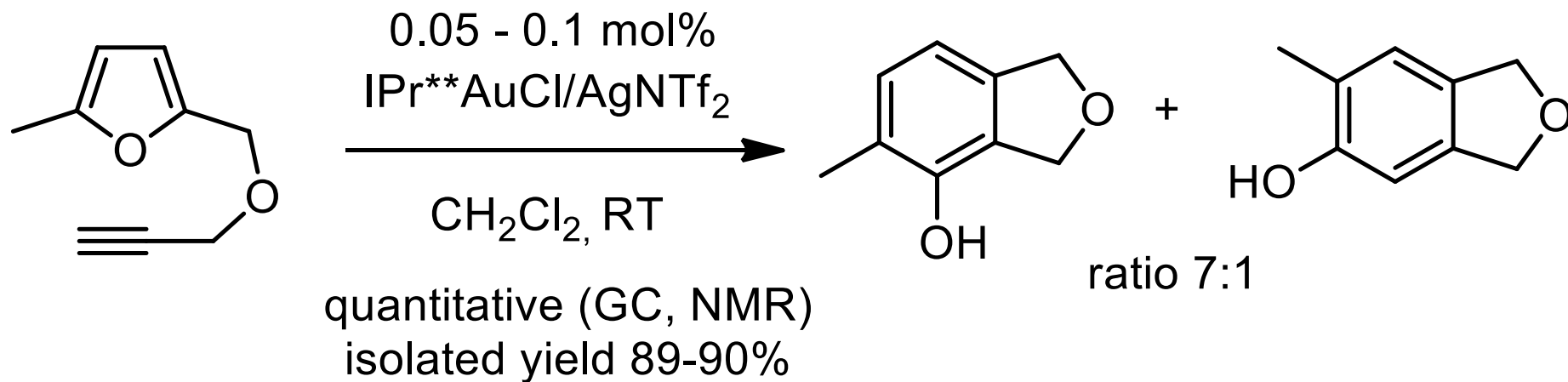


Gold as a Soft Proton



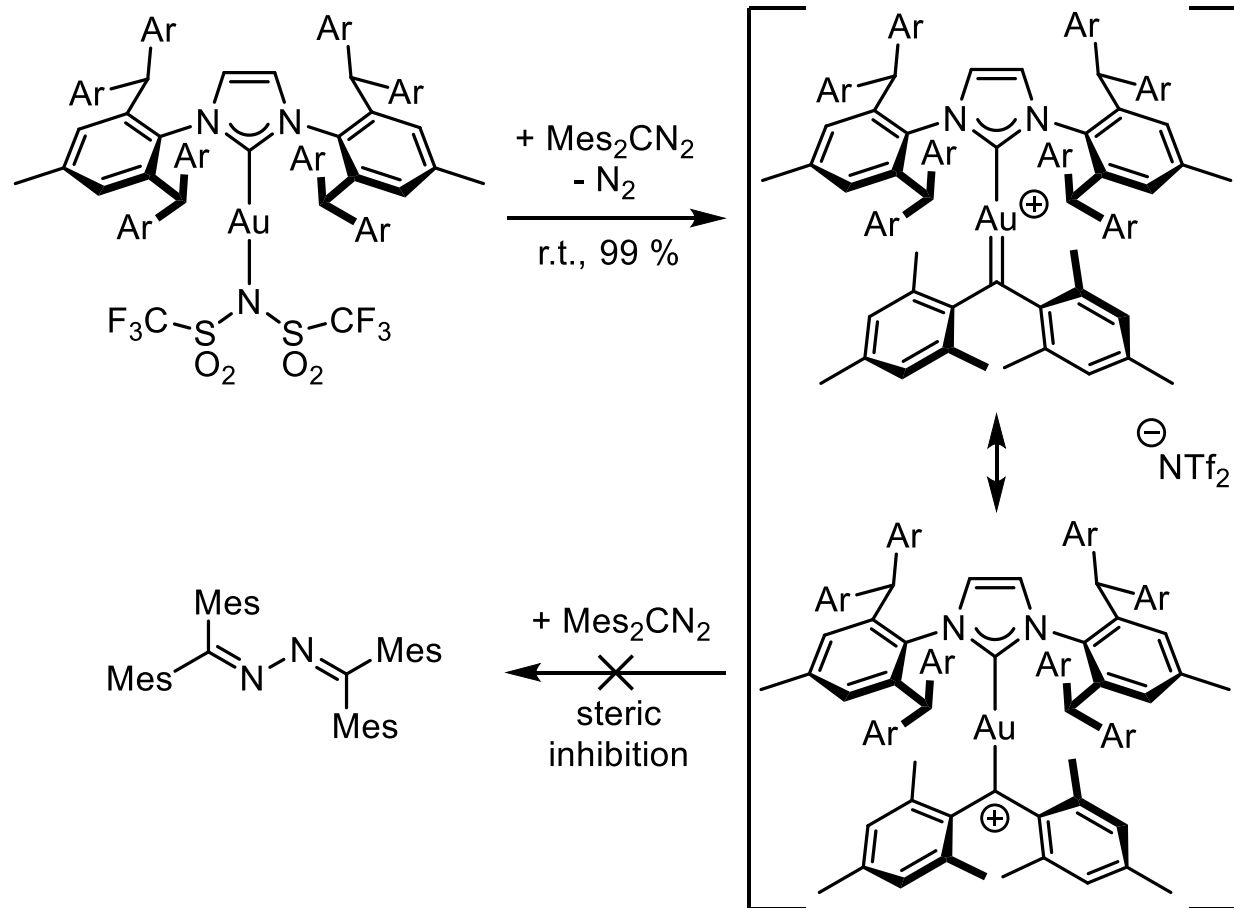


Unexpected Catalyst Activity and Stability

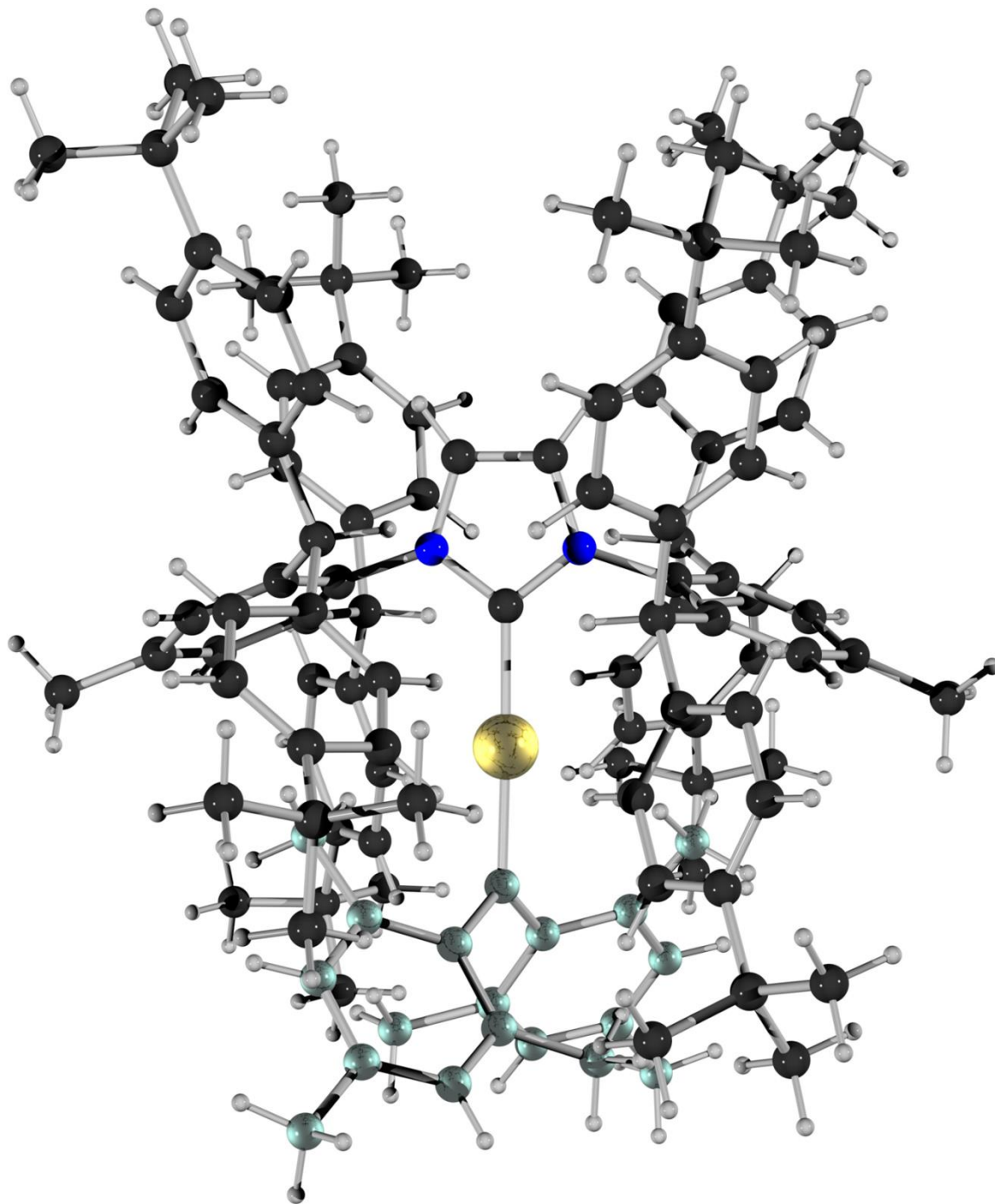


Simone G. Weber, David Zahner, Frank Rominger, Bernd F. Straub*,
ChemCatChem **2013**, 5, 2330-2335.

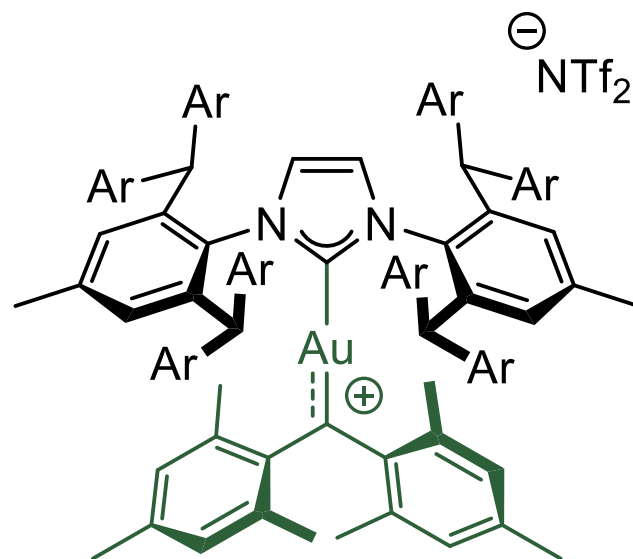
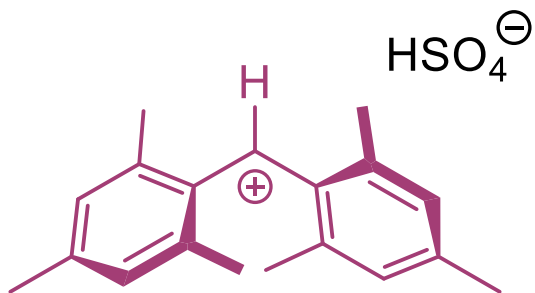
First Synthesis and Isolation of a „True“ Gold Carbene



Announced as „Hot Paper“: M. W. Hussong, F. Rominger, P. Krämer, B. F. Straub*, *Angew. Chem.* **2014**, 126, 9526; *Angew. Chem. Int. Ed.* **2014**, 53, 9372.

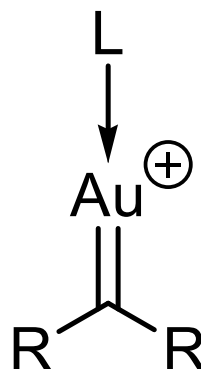


Gold is More Than a Fat, Soft Proton



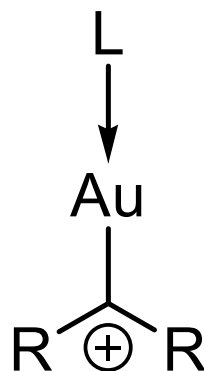
Gold Carbene Complexes or Gold Carbenoids?

Au=C Bond
Order 2



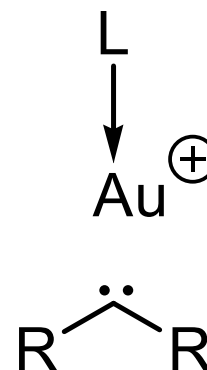
Back-Bonding

Au-C Bond
Order 1



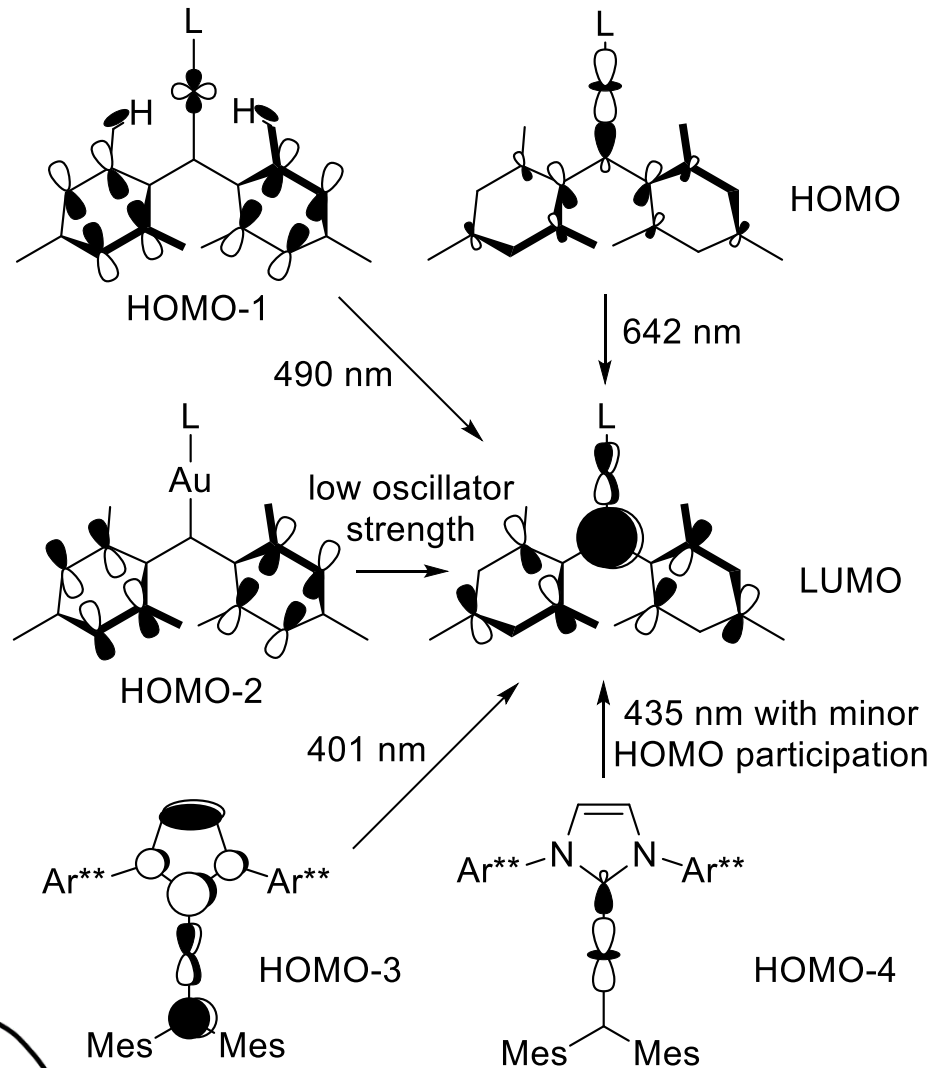
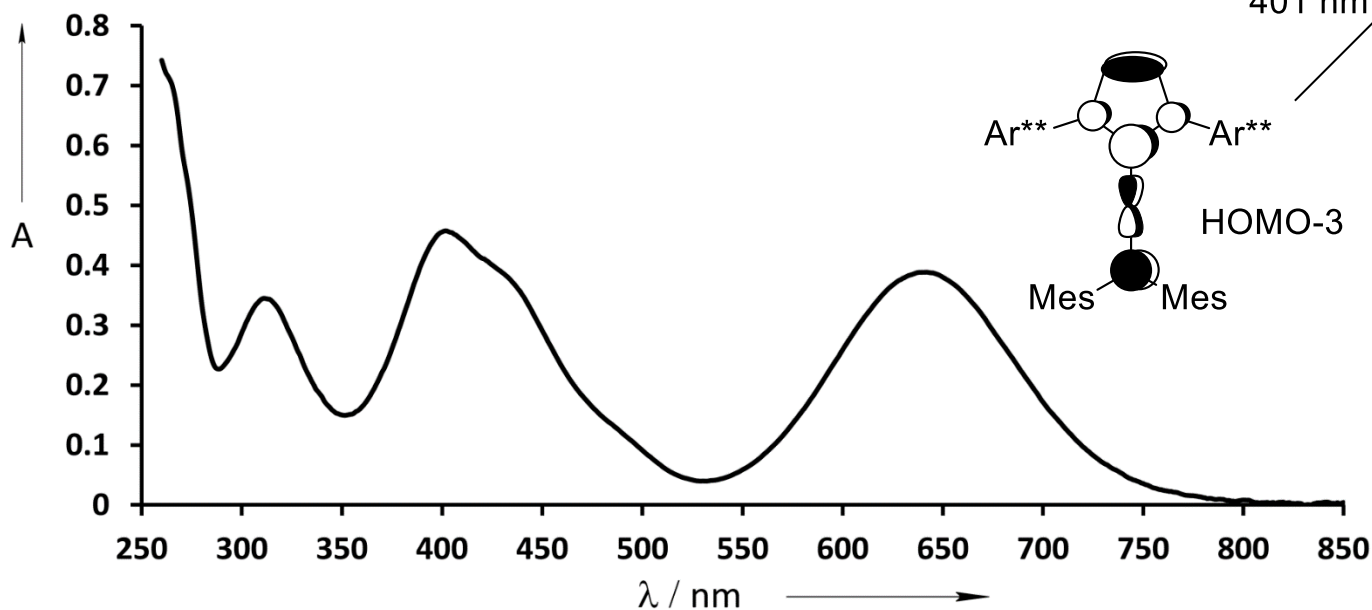
Carbenium

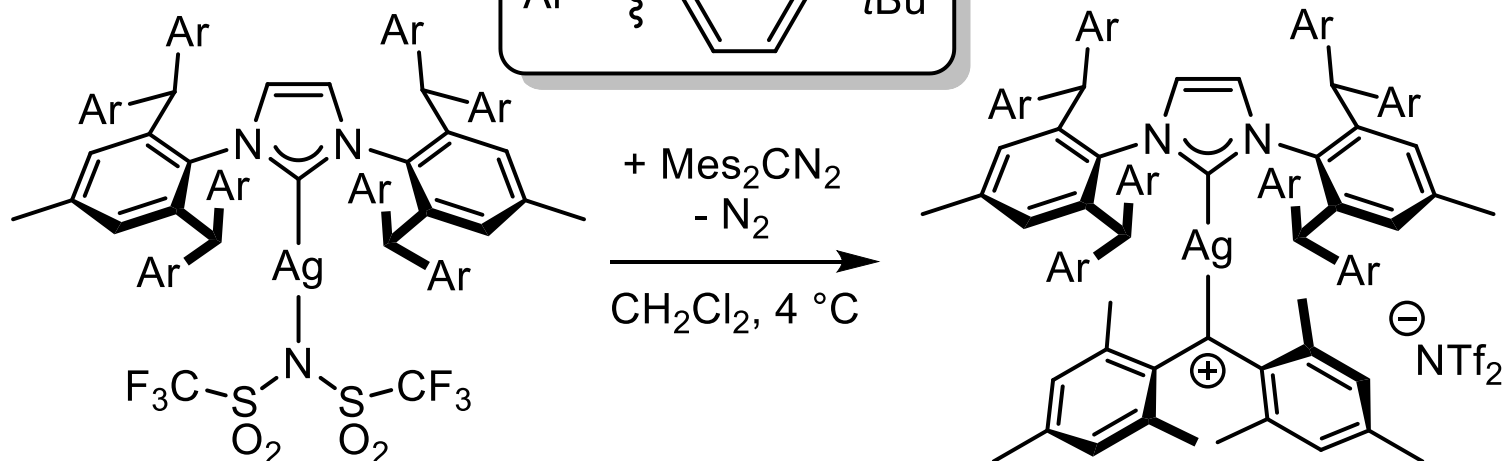
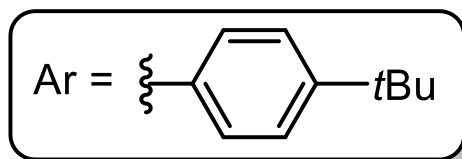
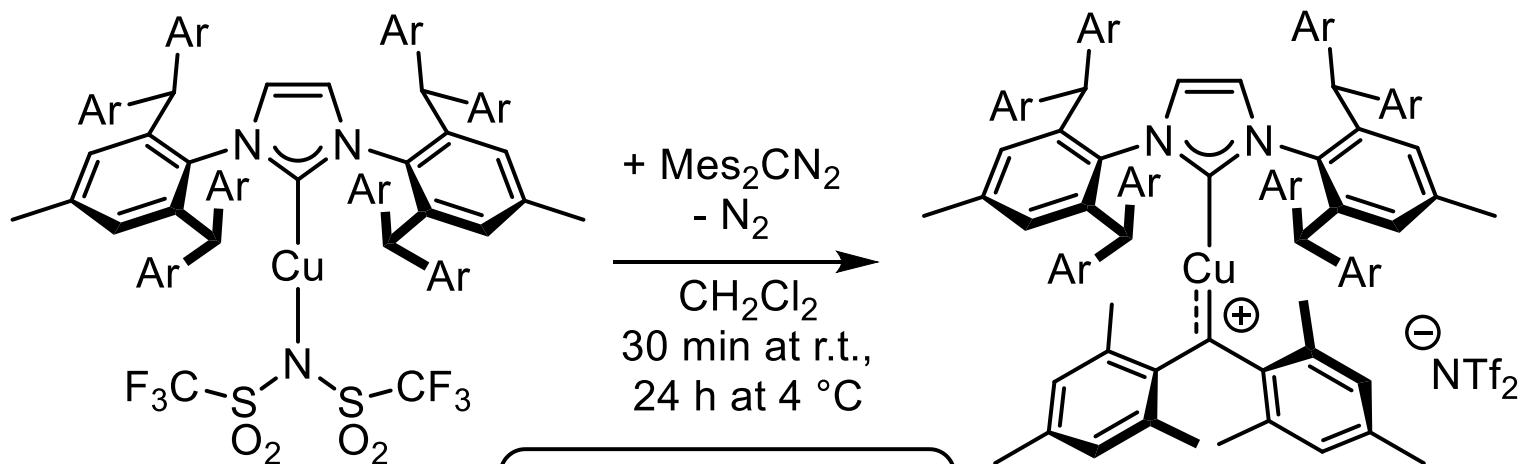
AuC Bond
Order 0



Carbenoid

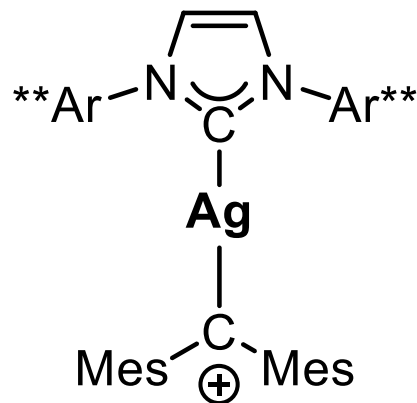
Four Visible Electronic Transitions



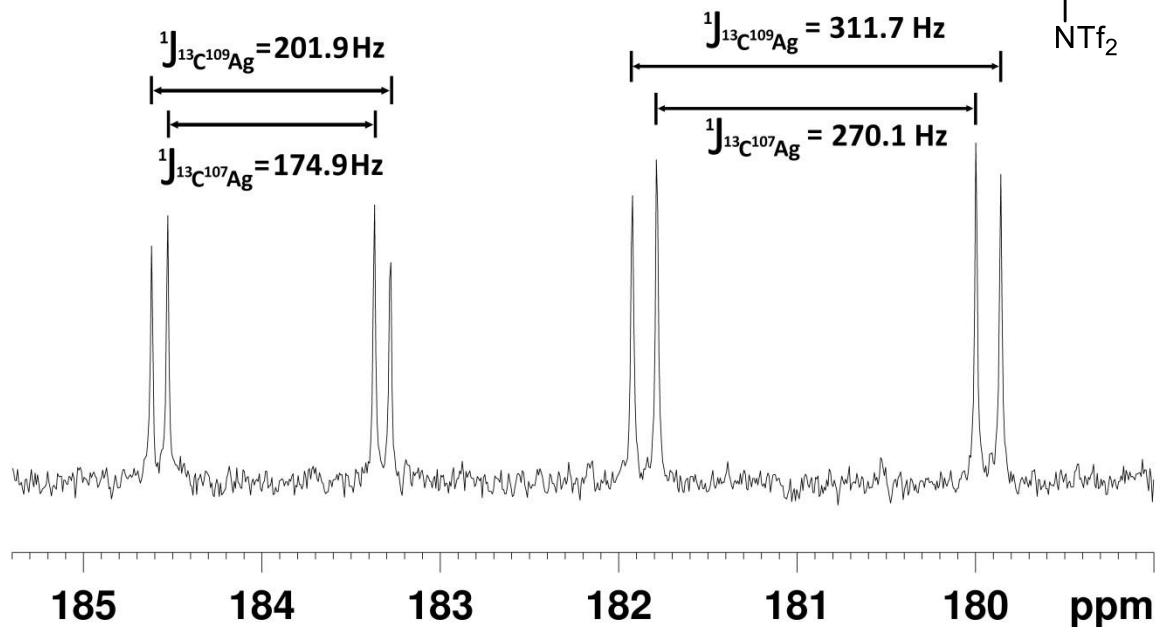
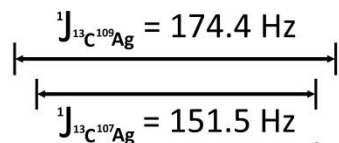
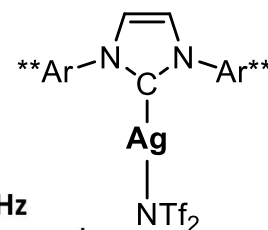


M. W. Hussong, W. T. Hoffmeister, F. Rominger, B. F. Straub*, *Angew. Chem.* **2015**, 127, DOI: 10472-10476; *Angew. Chem. Int. Ed.* **2015**, 54, 10331-10335, “hot paper”, front inside cover.

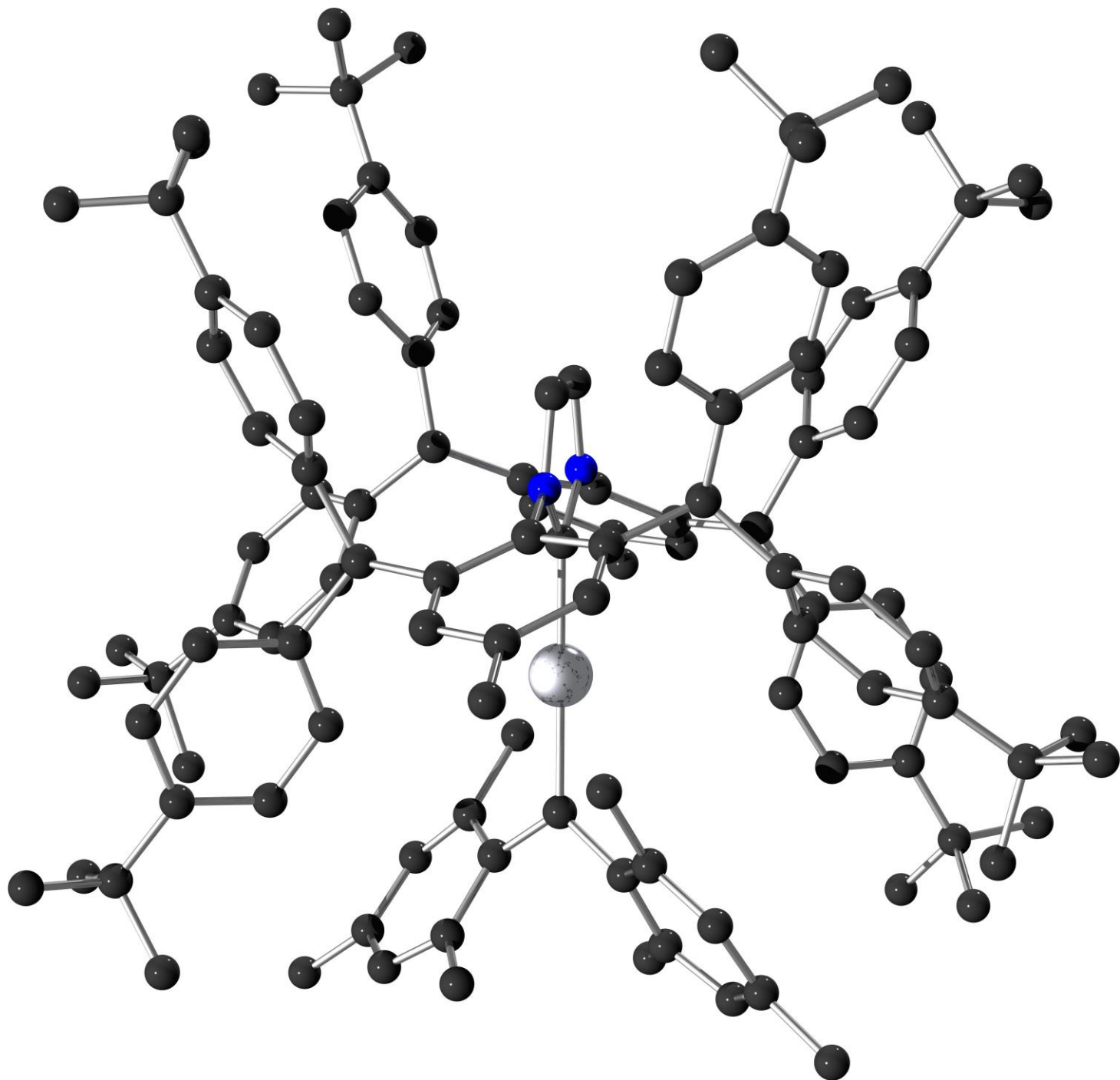
$^1J(^{13}\text{C}^{109}\text{Ag})$ and $^1J(^{13}\text{C}^{107}\text{Ag})$



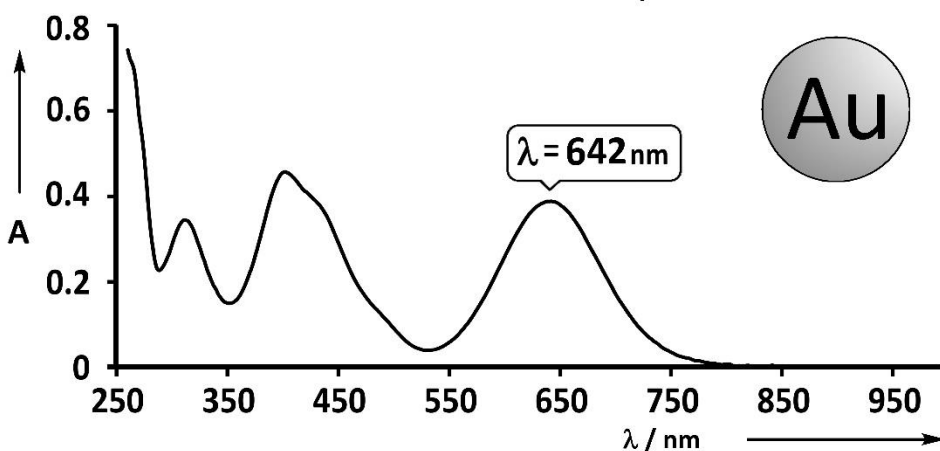
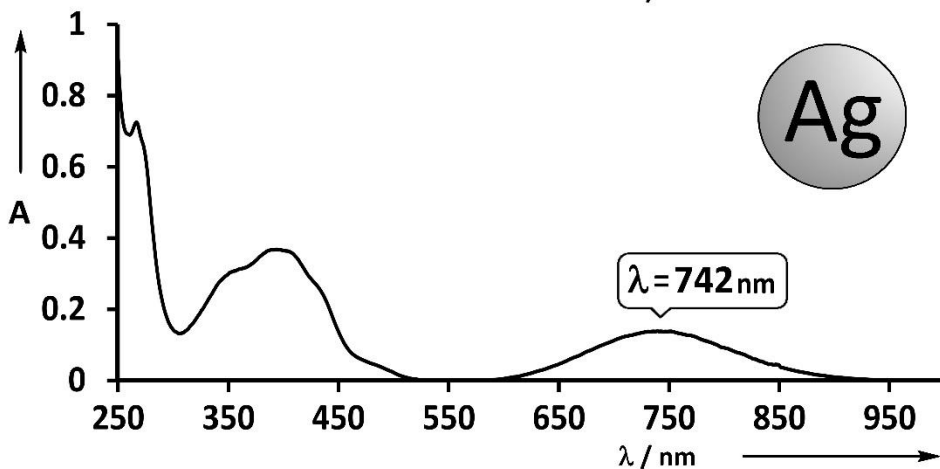
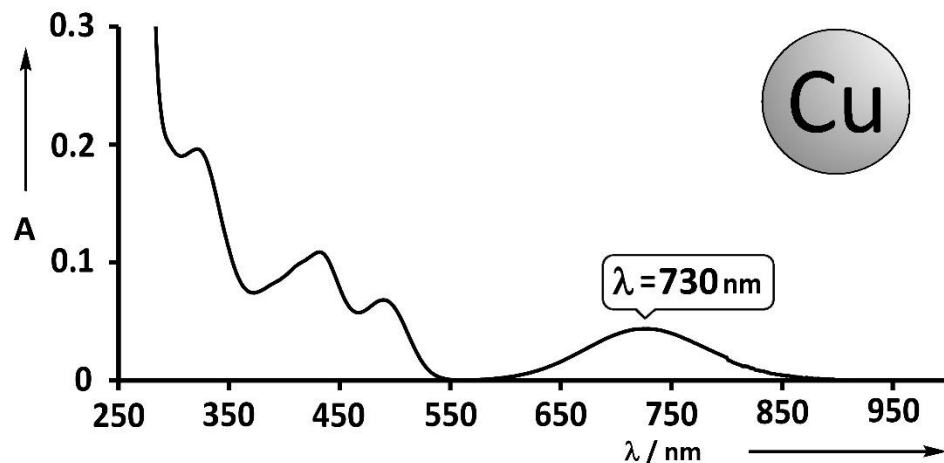
MH 83B T=283K

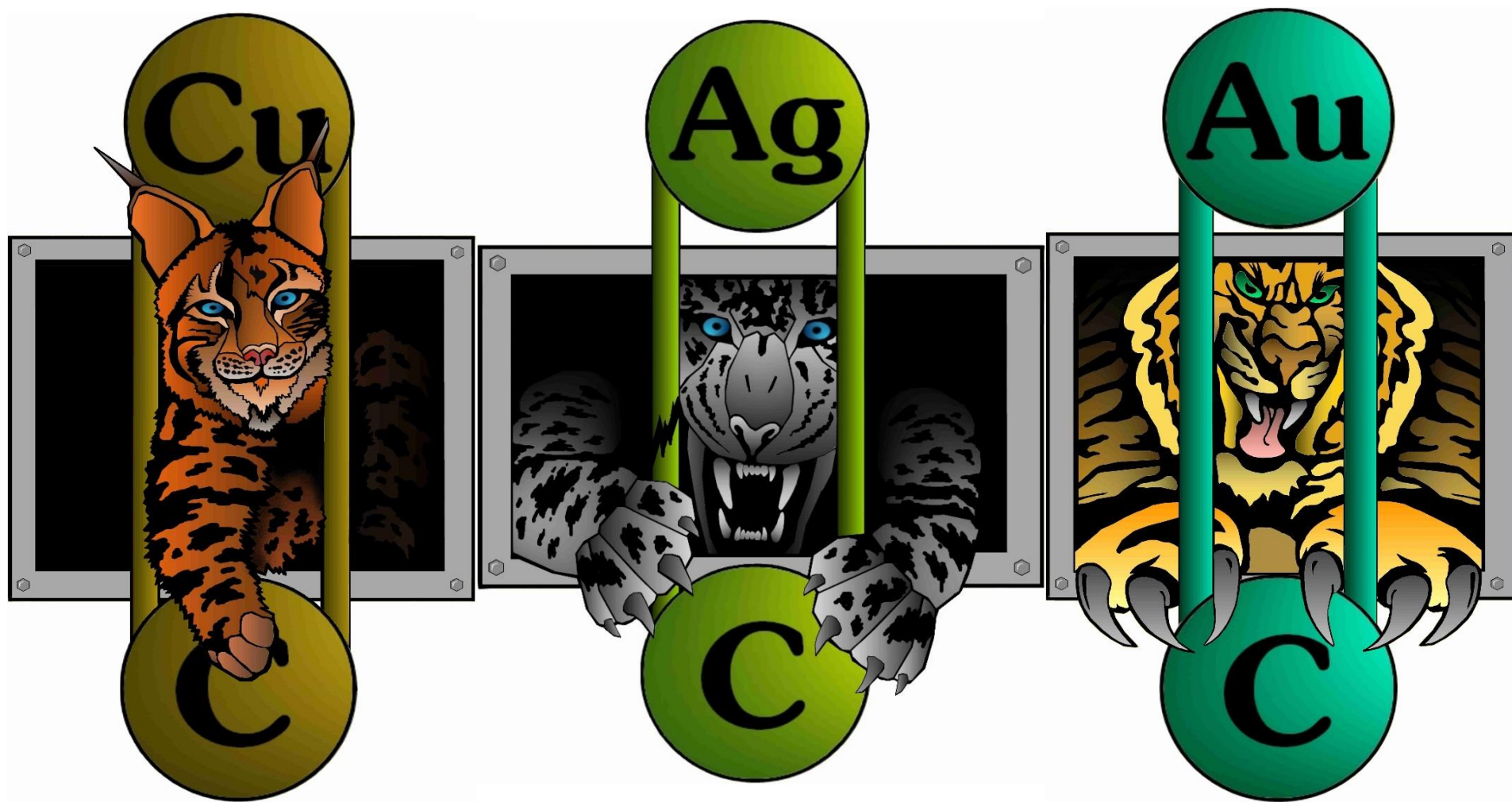


MH 83B T=283K



UV/Vis Spectra: Seeing is Believing





Goals

- IPr** gold complex with carbene fragment reactive towards small substrates
- IPr** complexes of other late transition metals

Novel Ligand tailored for industrial catalysis

- Chemically and thermally stable ancillary ligand for high turn-over number TON
- Straightforward and cheap ligand synthesis
- Earth-abundant metals



Acknowledgment of Financial Support



Studienstiftung
des deutschen Volkes



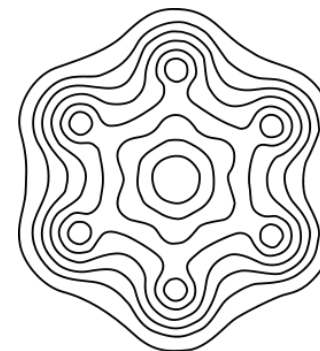
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