

Reaktionsmechanismen und Katalyse-Intermediate



Forschungskolloquium der Chemischen Institute

20.11.2014

Prof. Dr. Bernd F. Straub

Organisch-Chemisches Institut

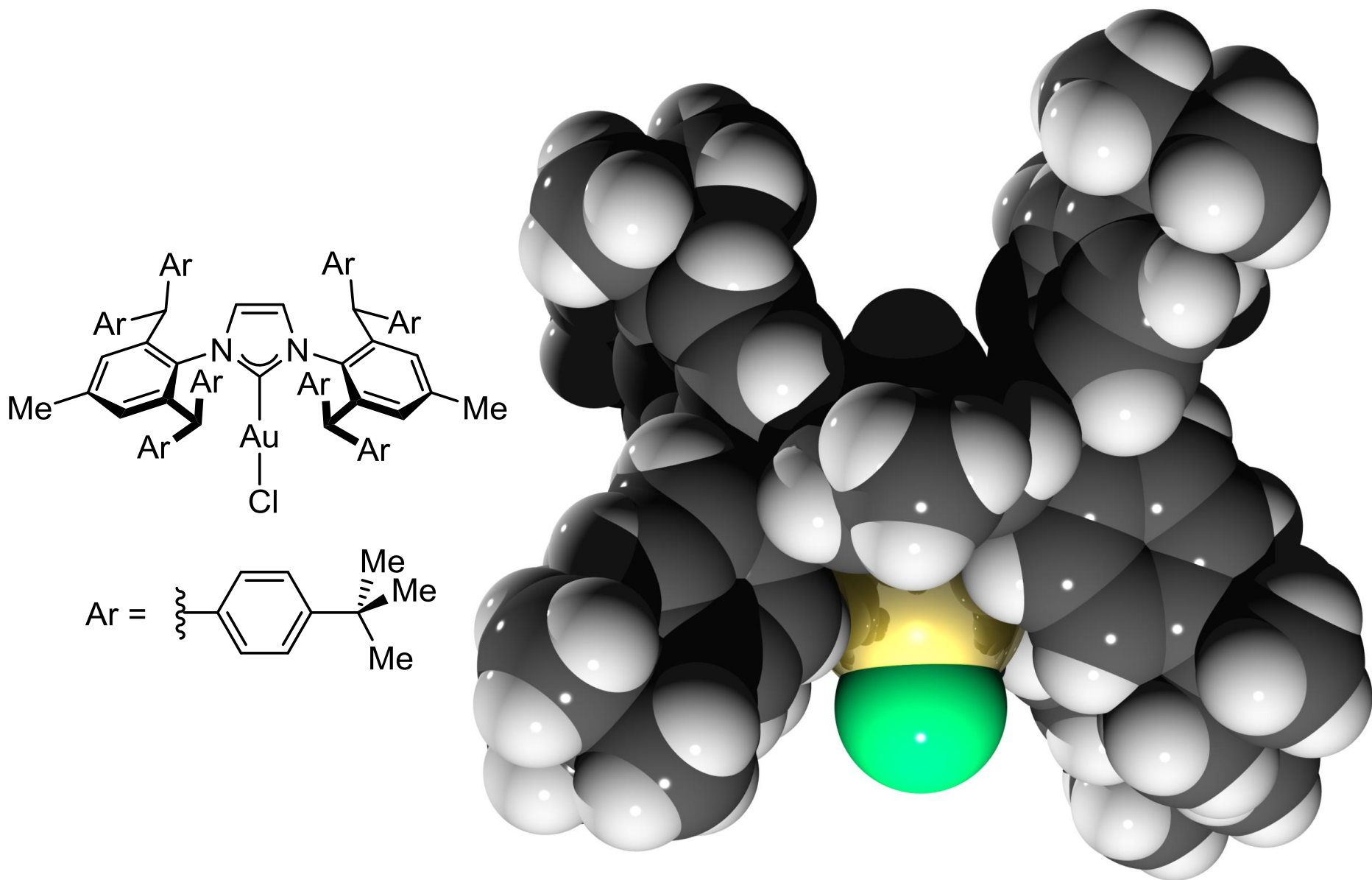
Universität Heidelberg

Content

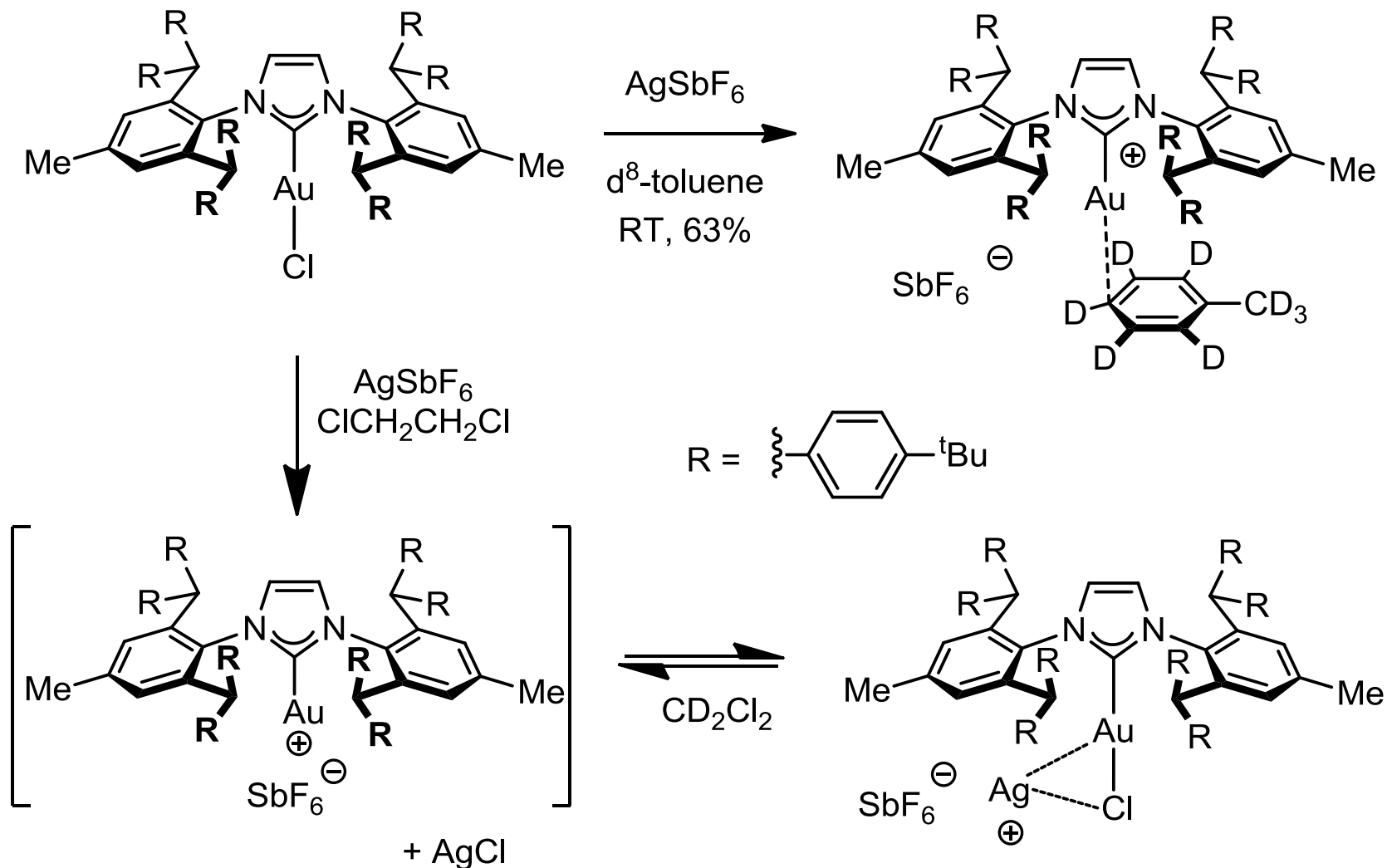
- 1) Isolation of reactive Gold Intermediates
- 2) Environmentally benign lipophilic Anions
- 3) Highly active CuAAC „Click“ Catalysts

Isolation of Reactive Gold Intermediates

Sterically Shielded Ancillary Ligand

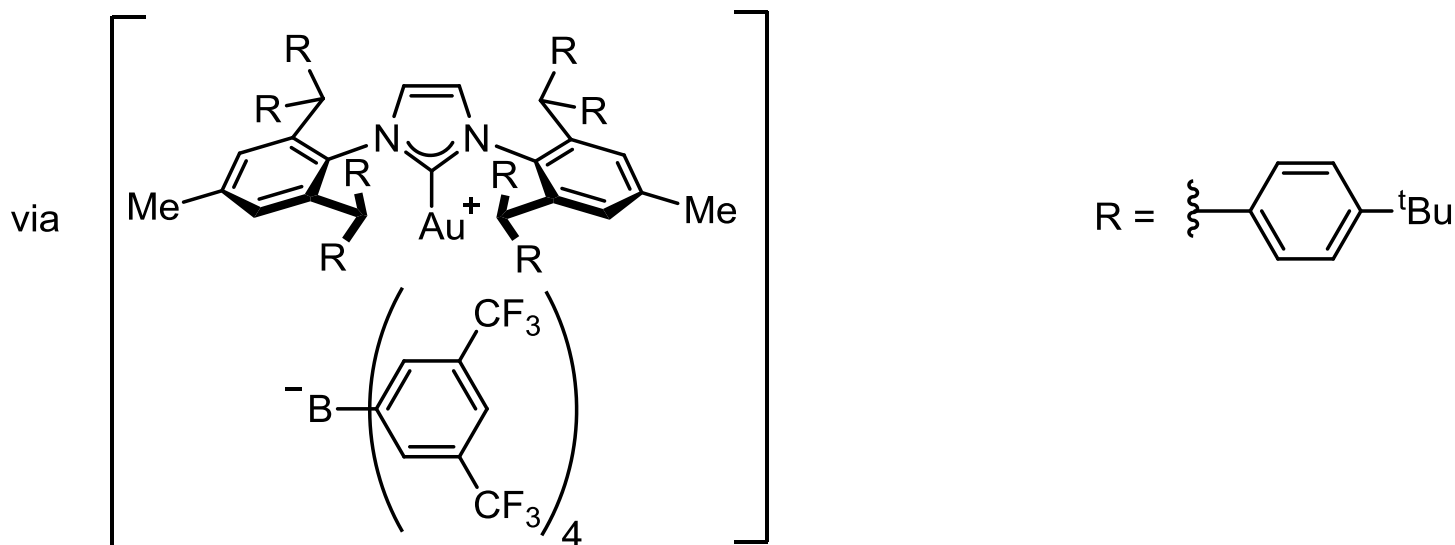
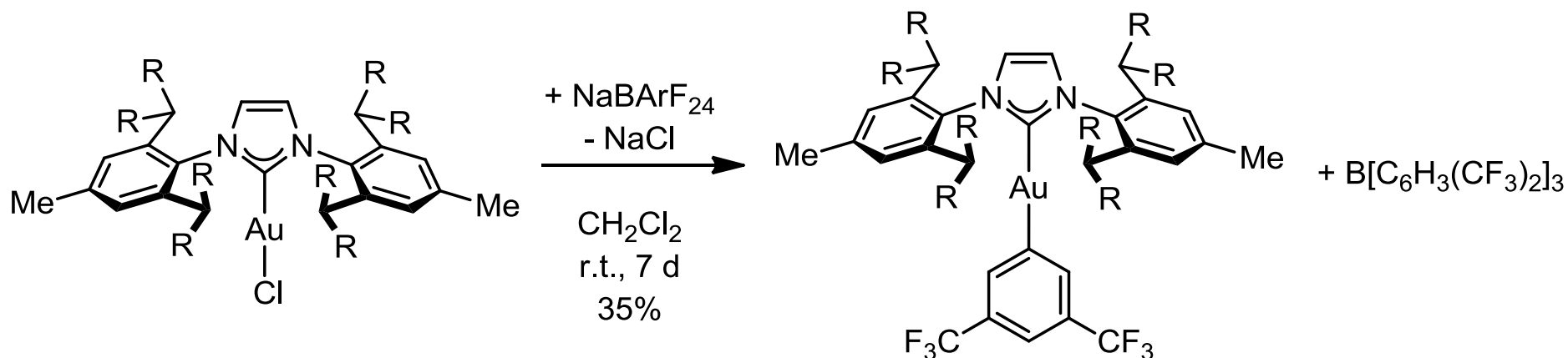


Silver Caught Red-Handed

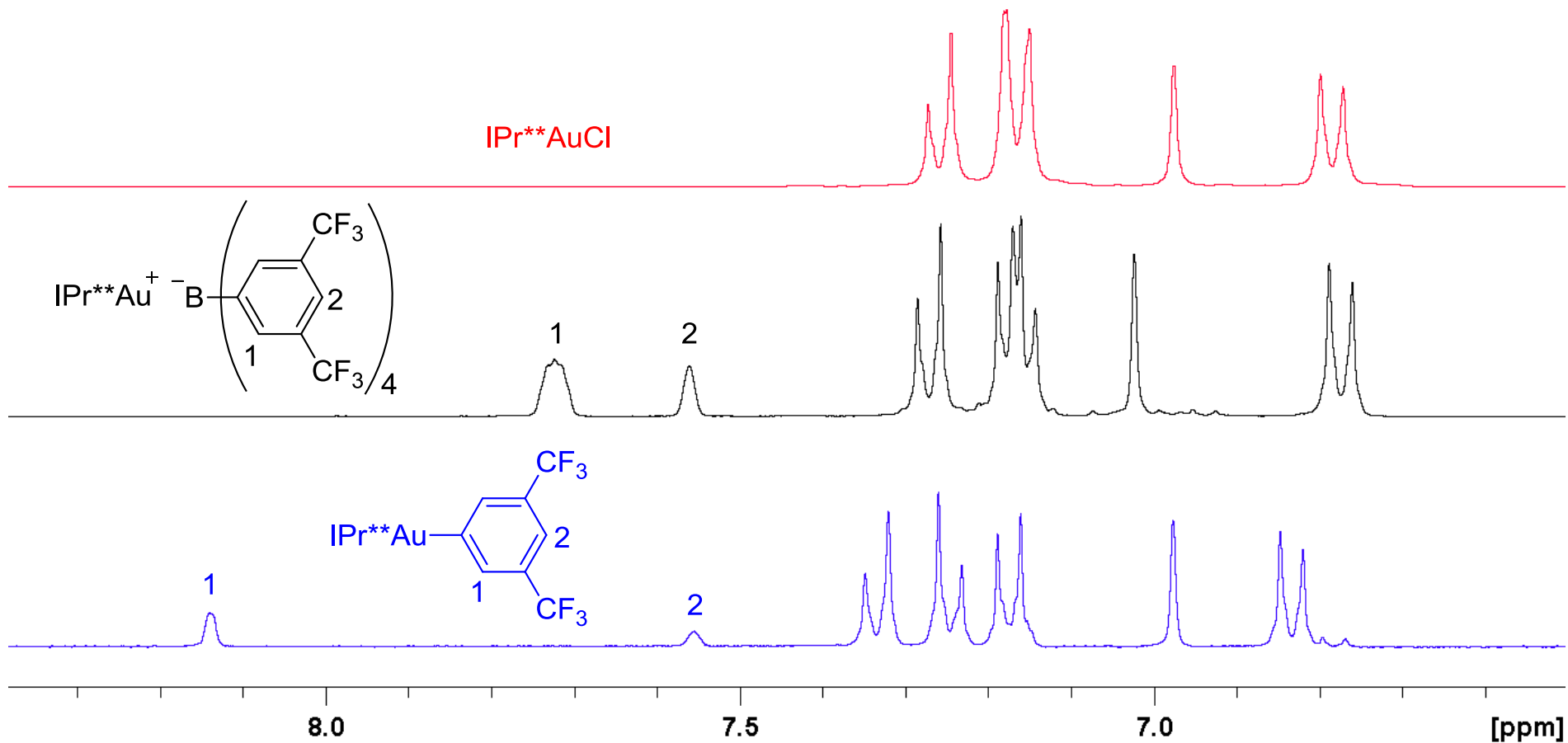


Simone G. Weber, Frank Rominger, Bernd F. Straub*,
Eur. J. Inorg. Chem. **2012**, 2863-2867.

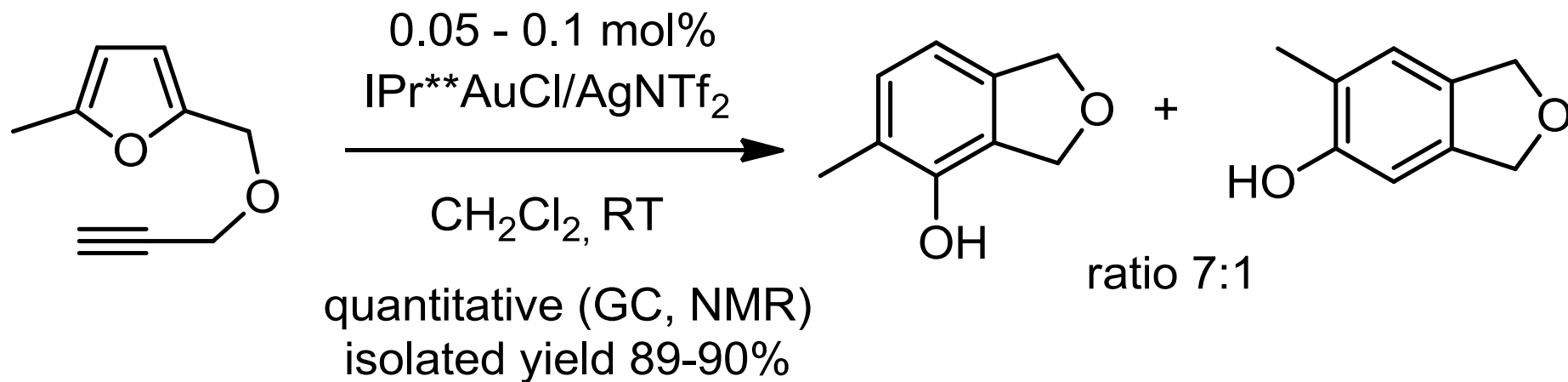
Gold as a Soft Proton



Rapid Chloride Abstraction – Clean BArF₂₄ Activation

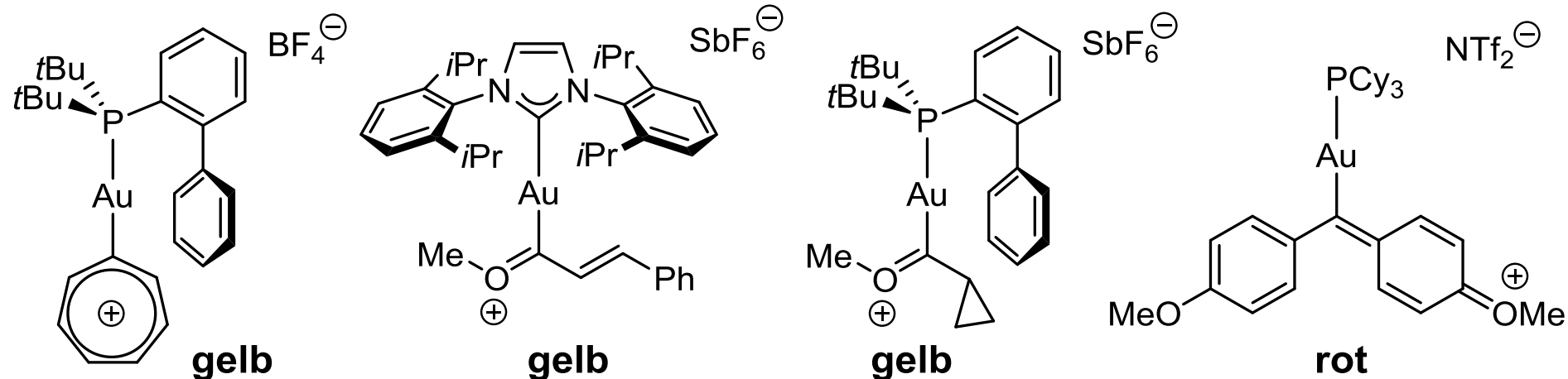


Unexpected Catalyst Activity and Stability



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

Gold Carbenoids in the Literature

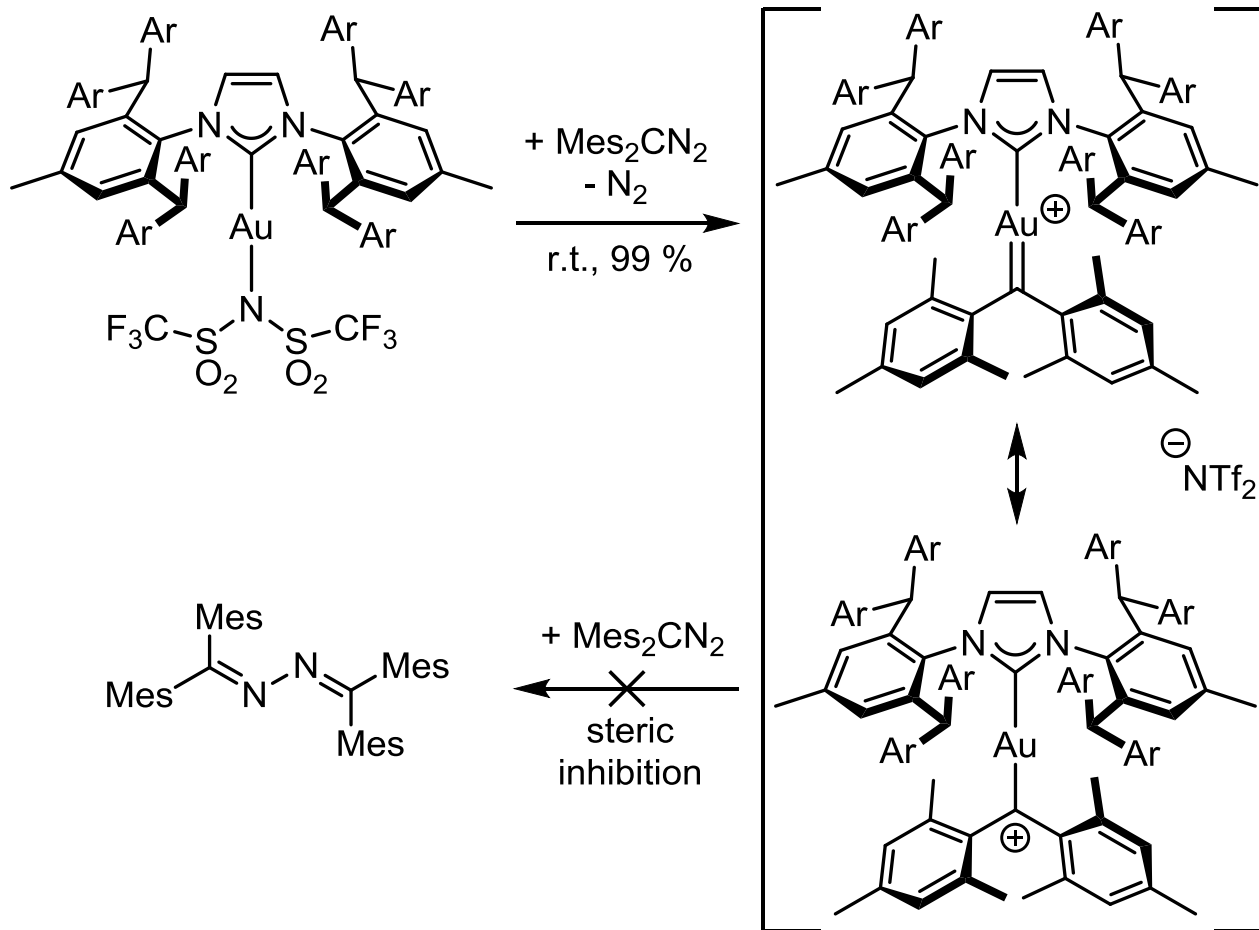


- a) R. J. Harris, R. A. Widenhoefer, *Angew. Chem. Int. Ed.* **2014**, 53, 9369;
 b) M. Fañanàs-Mastral, F. Aznar, *Organometallics* **2009**, 28, 666-668;
 c) R. E. M. Brooner, R. A. Widenhoefer, *Chem. Commun.* **2014**, 50, 2420-2423;
 d) G. Seidel, A. Fürstner, *Angew. Chem.* **2014**, 126, 4907-4911;
Angew. Chem. Int. Ed. **2014**, 53, 4807-4811.



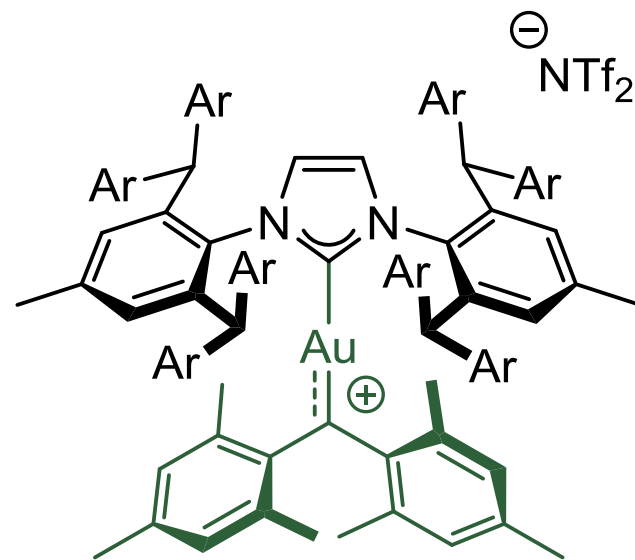
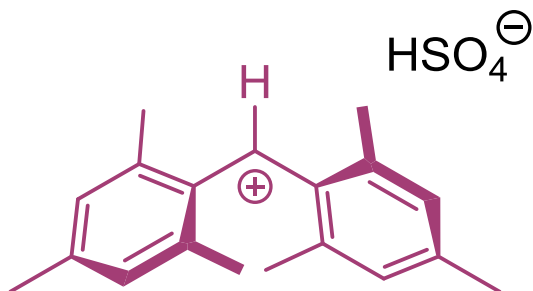
© Matthias Hussong

First Synthesis and Isolation of a „True“ Gold Carbene

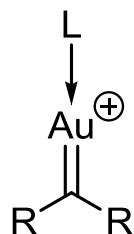


Announced as „Hot Paper“: M. W. Hussong, F. Rominger, P. Krämer, B. F. Straub, *Angew. Chem.* **2014**, 126, 9526; *Angew. Chem. Int. Ed.* **2014**, 53, 9372. 11

Gold is much more than just a fat, soft Proton

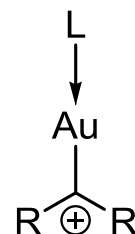


Au=C Bond
Order 2



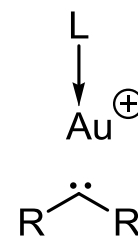
Back-Bonding

Au-C Bond
Order 1



Carbenium

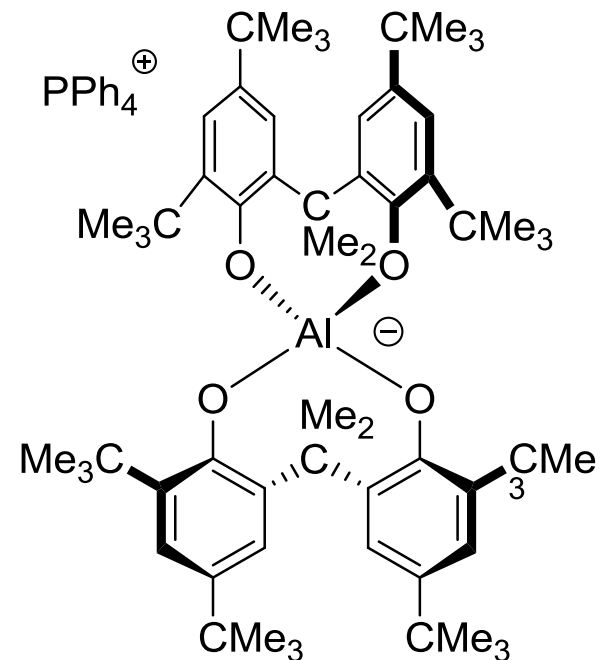
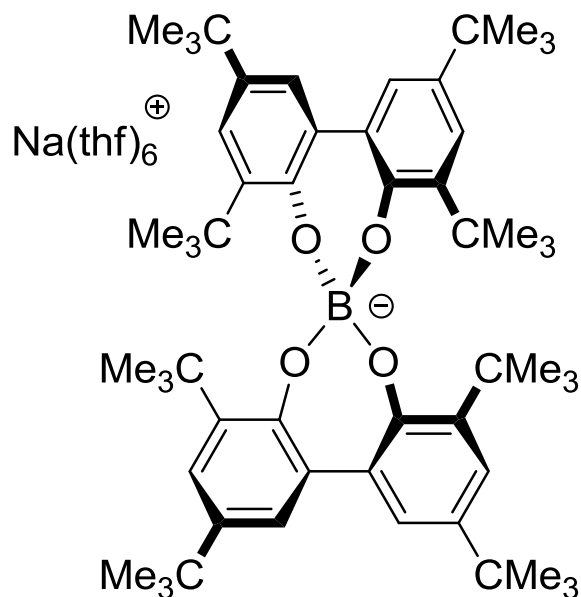
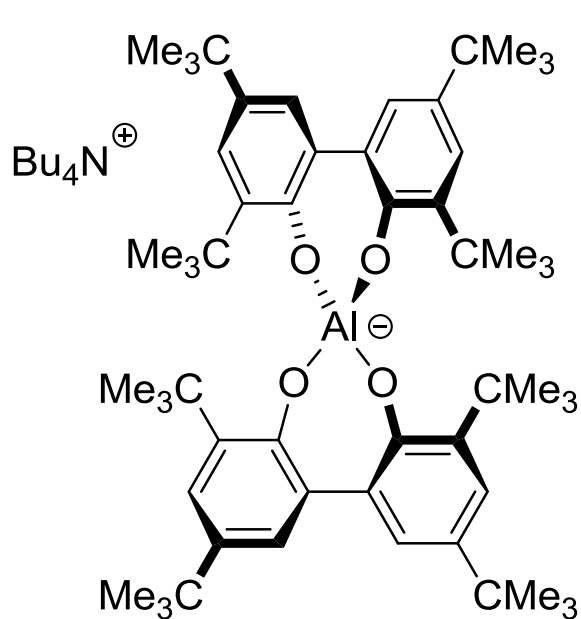
AuC Bond
Order 0



Carbenoid

Environmentally Benign Lipophilic Anions

Unprecedented Solubility



solubility of 33 g/L
in pentane at r.t.

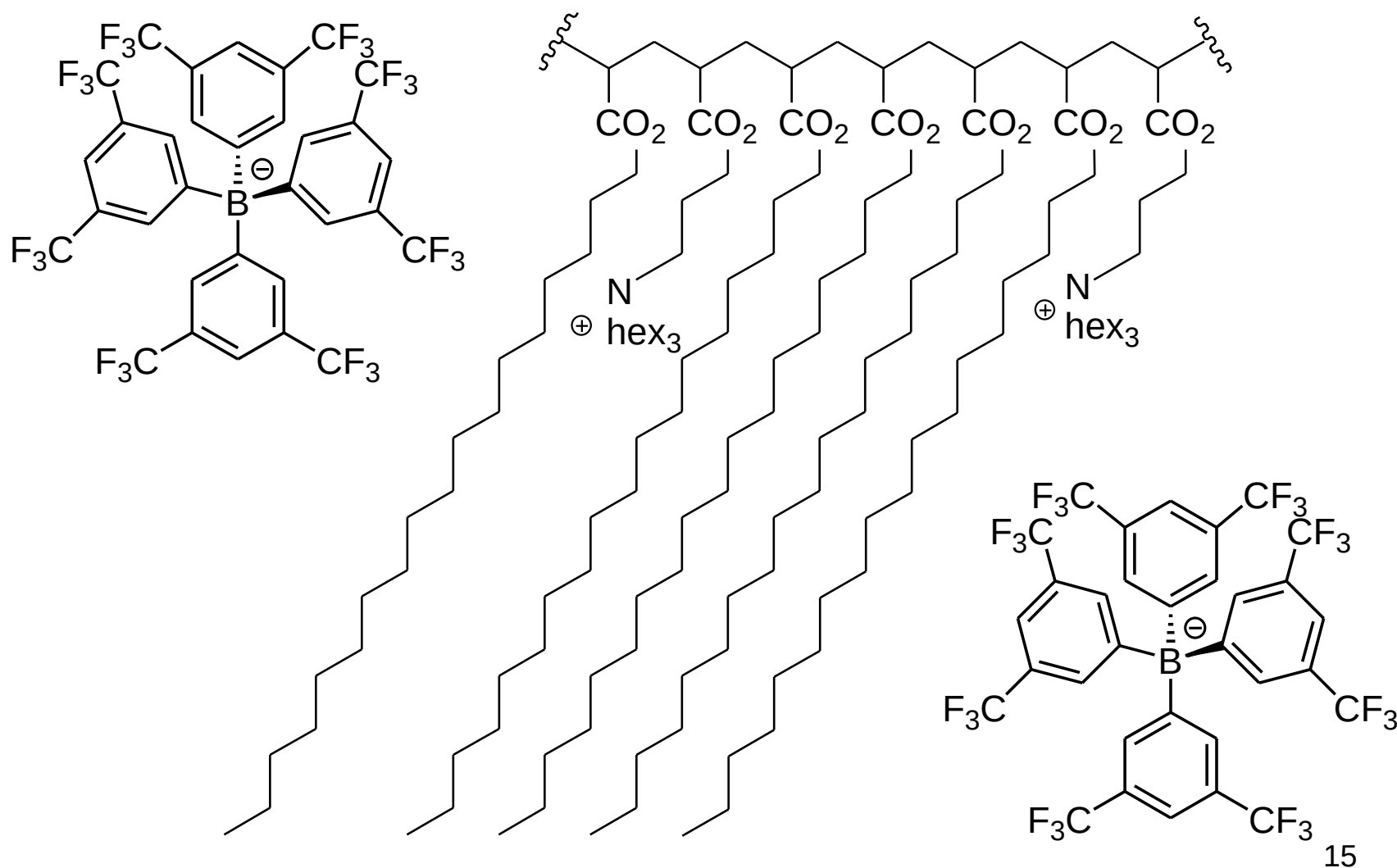
Bernd F. Straub*, Michael Wrede, Karin Schmid, Frank Rominger,
Eur. J. Inorg. Chem. **2010**, 1907-1911.

Michael Wrede, Viktoria Ganza, Gerald K. Kannenberg, Frank Rominger, Bernd F. Straub*, *Inorganica Chimica Acta* **2011**, 369, 71-75.

Timo Söhner, Ina K. Küppers, Wiebke Wackerow, Frank Rominger,
Bernd F. Straub*, *Arkivoc* **2014**, 4, 296-318.

Why Lipophilic Anions?

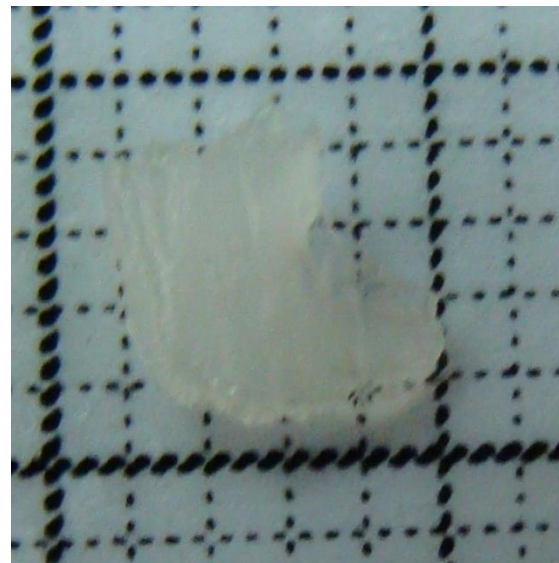
Superabsorber for Organic Solvents



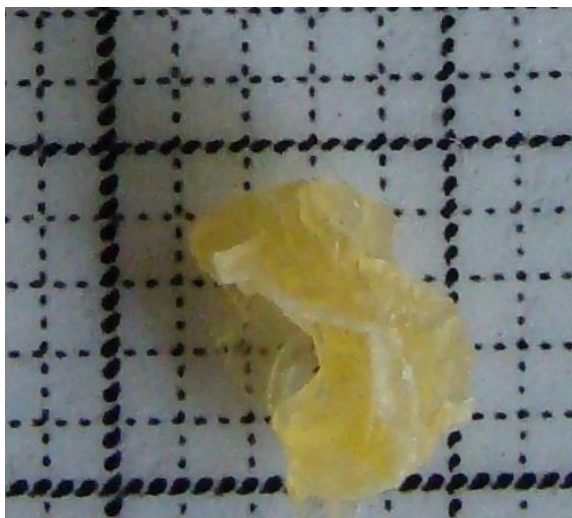
T. Ono, T. Sugimoto, S. Shinkai, K. Sada, *Nature Materials* **2007**, 6, 429.

Superabsorber for Diesel Fuel

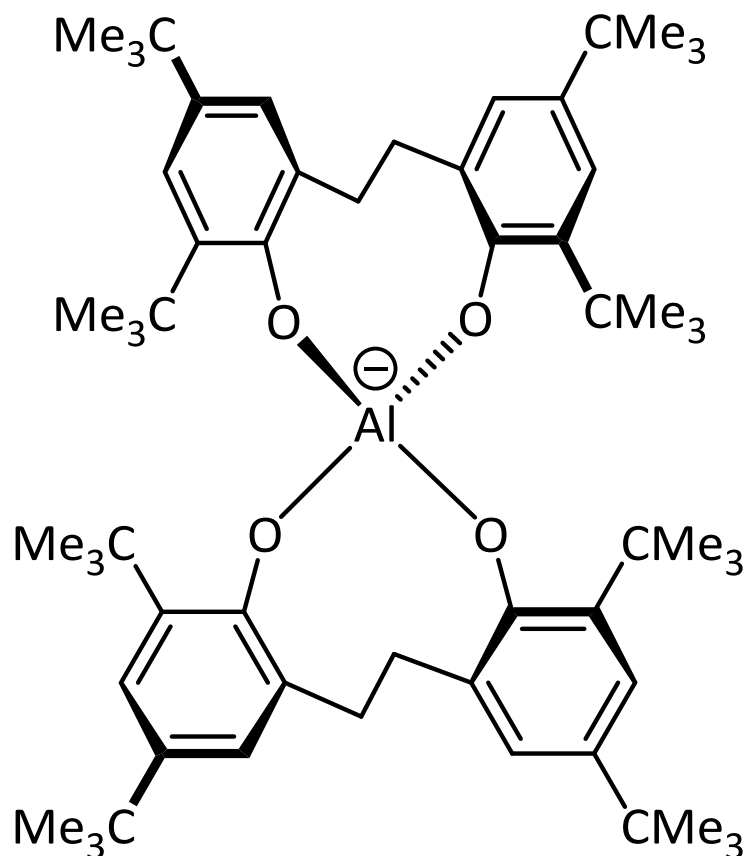
NG18 in Diesel



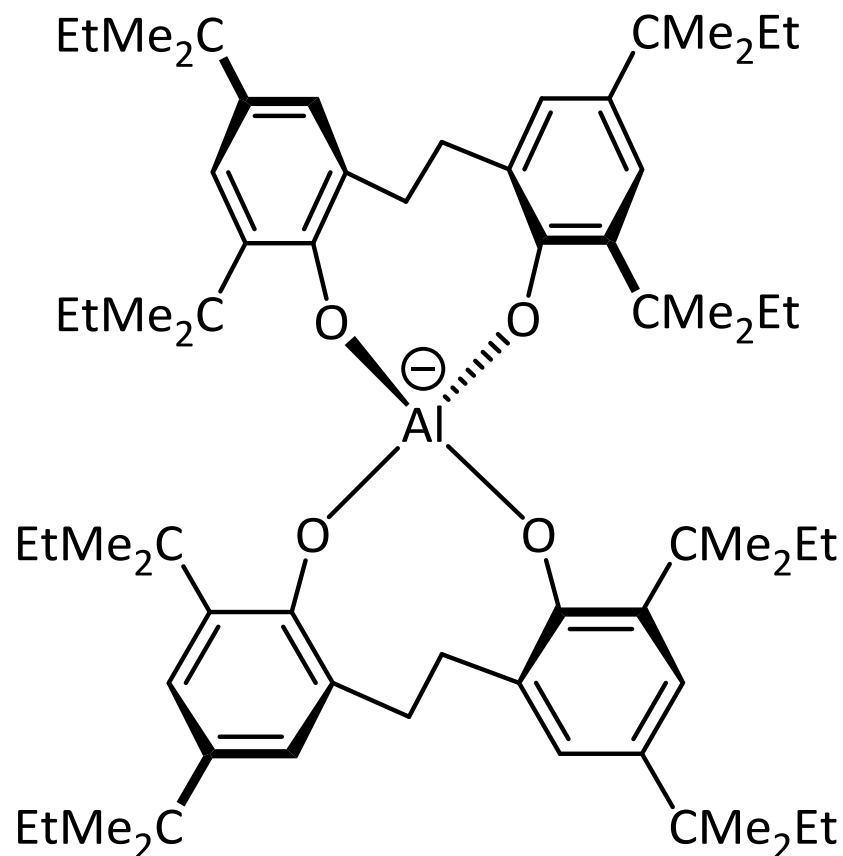
EG18-Altebat
in Diesel



Water-Stable, Lipophilic Aluminate Ester Anions

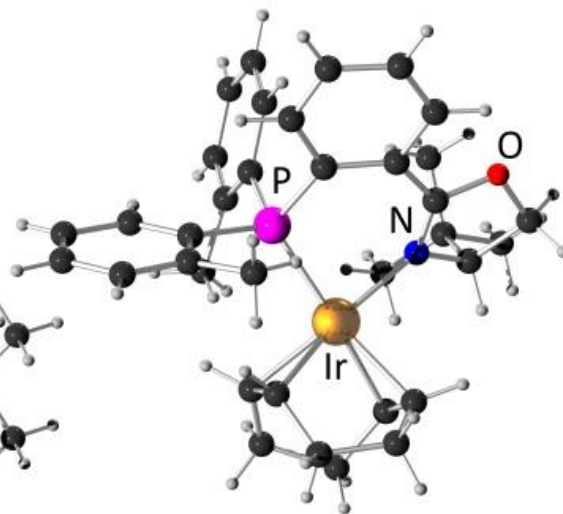
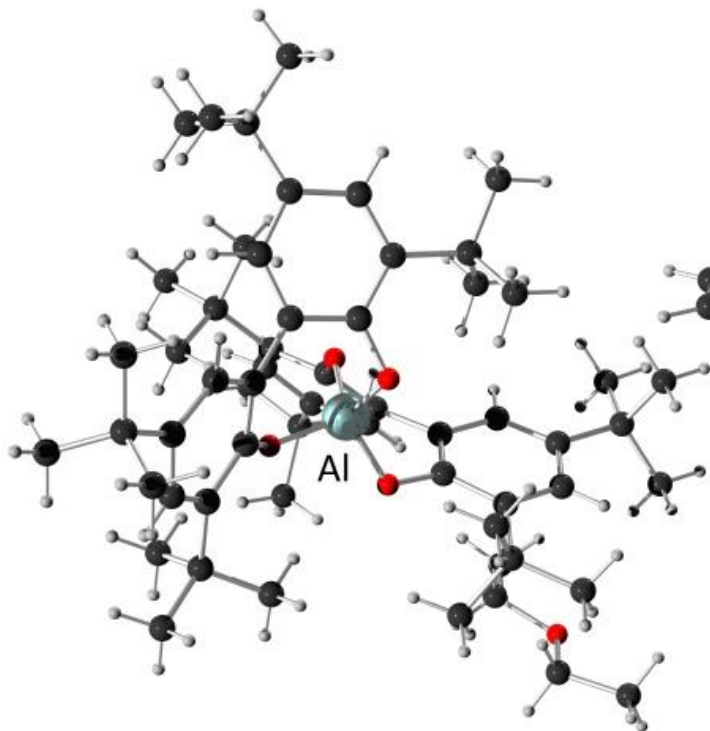
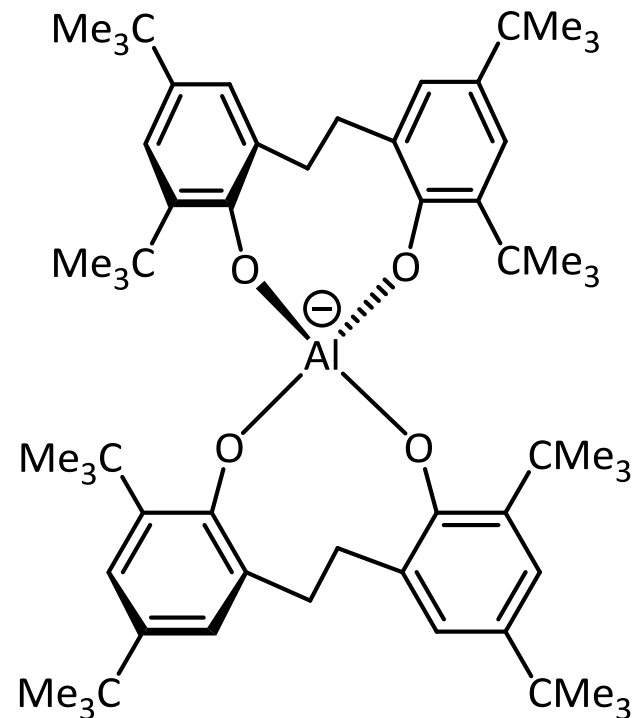
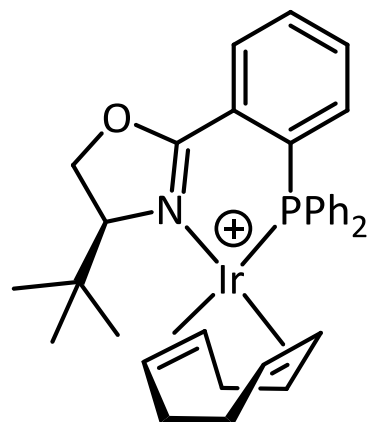
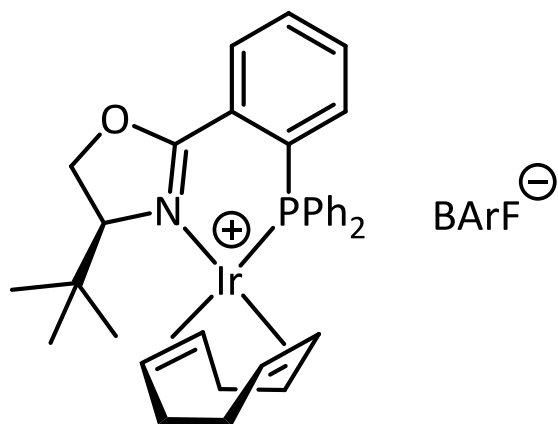


"Aletbat"
high tendency
of crystallization



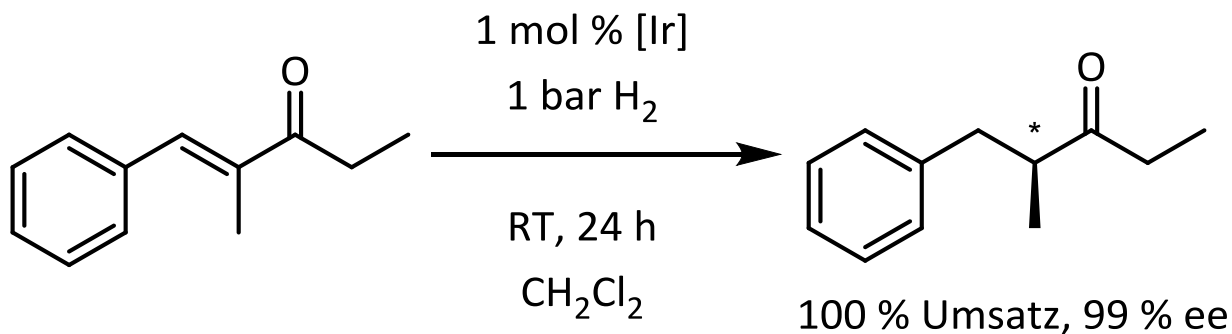
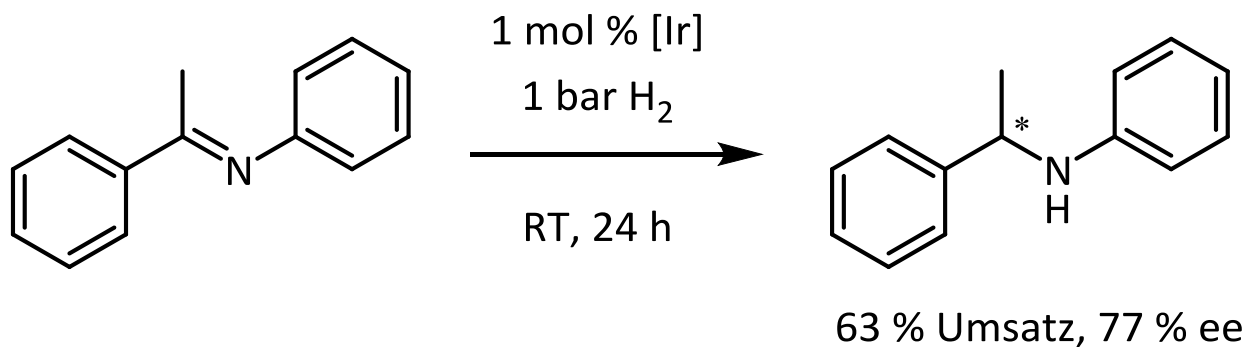
"Aletpat"
high solubility in
hydrocarbons

S.-M. Lu, C. Bolm,
Angew. Chem. Int. Ed. **2008**,
 47, 8920-8923.



Timo Söhner, Felix Braun,
 Lena Charlotte Over, Sven
 Mehlhose, Frank Rominger,
 Bernd F. Straub*, *Green
 Chem.* **2014**, 4696-4707.

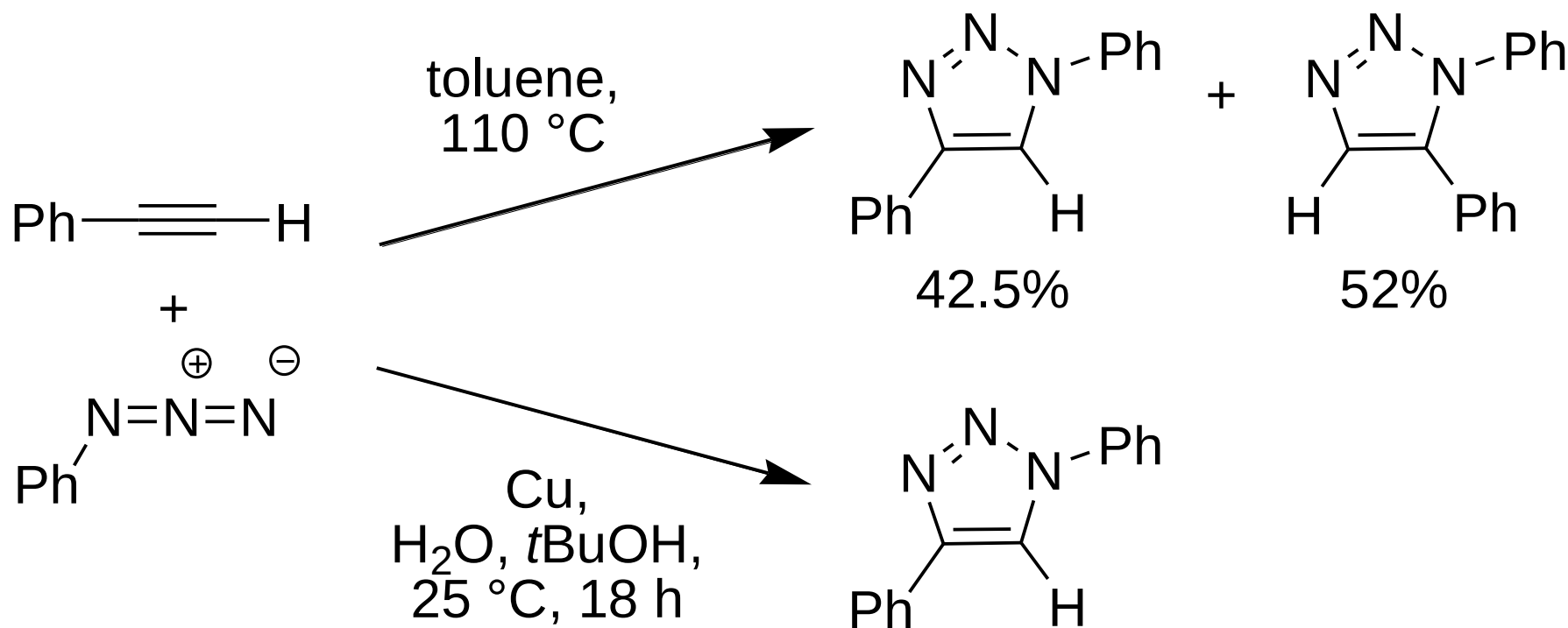
Hydrogenation Catalysis



Timo Söhner, Felix Braun, Lena Charlotte Over, Sven Mehlhose, Frank Rominger, Bernd F. Straub*, *Green Chem.* **2014**, 4696-4707.

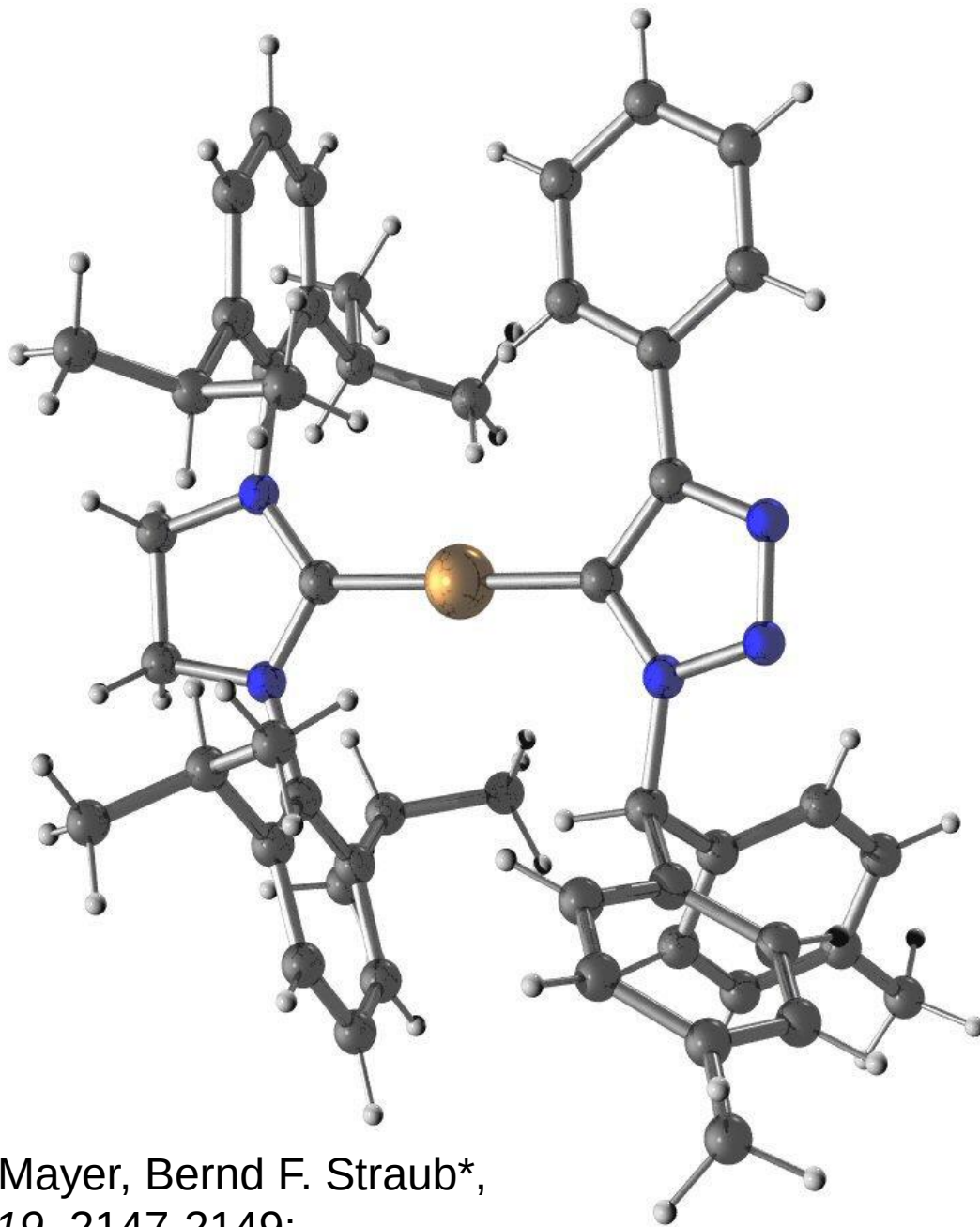
Highly Active CuAAC „Click“ Catalysts

Traditional Huisgen Cycloaddition, and CuAAC Reaction



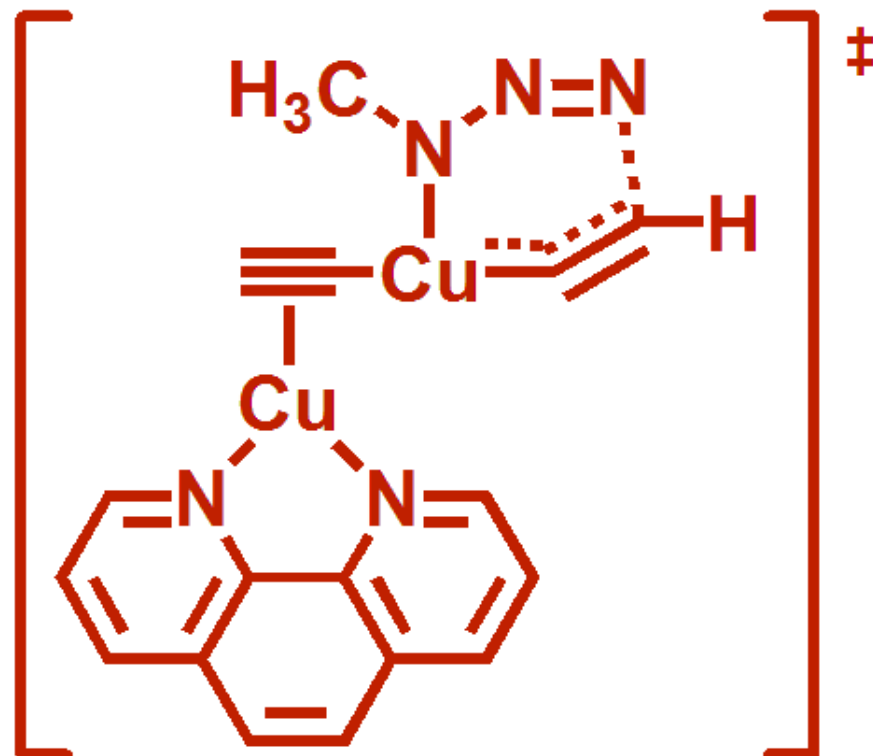
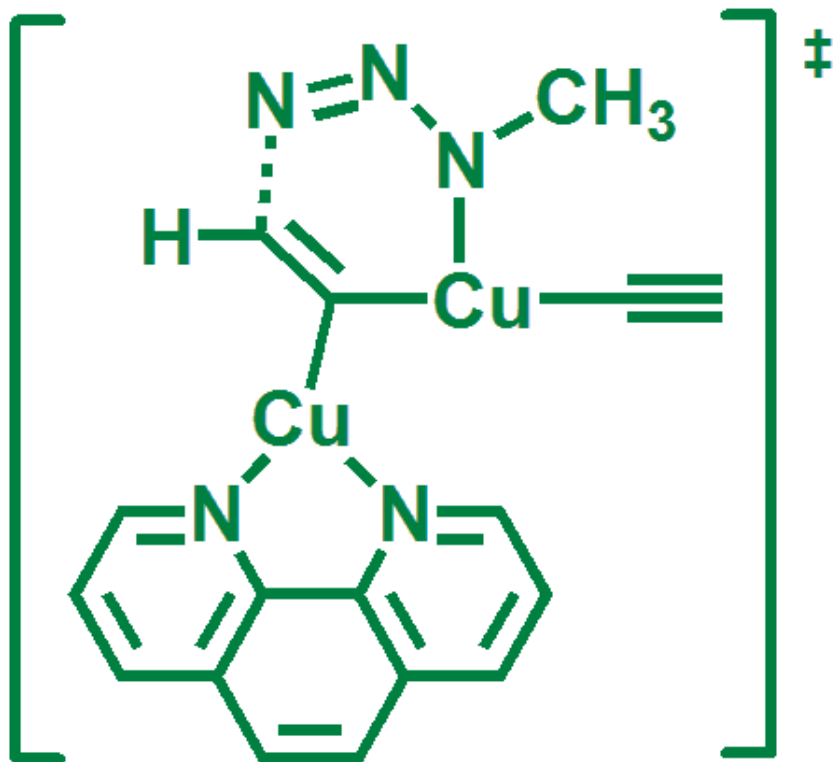
a) W. Kirmse, L. Horner, *Liebigs Ann. Chem.* **1958**, 614, 1;

b) L. D. Pachon, J. H. van Maarseveen, G. Rothenberg, *Adv. Synth. Catal.* **2005**, 347, 811.

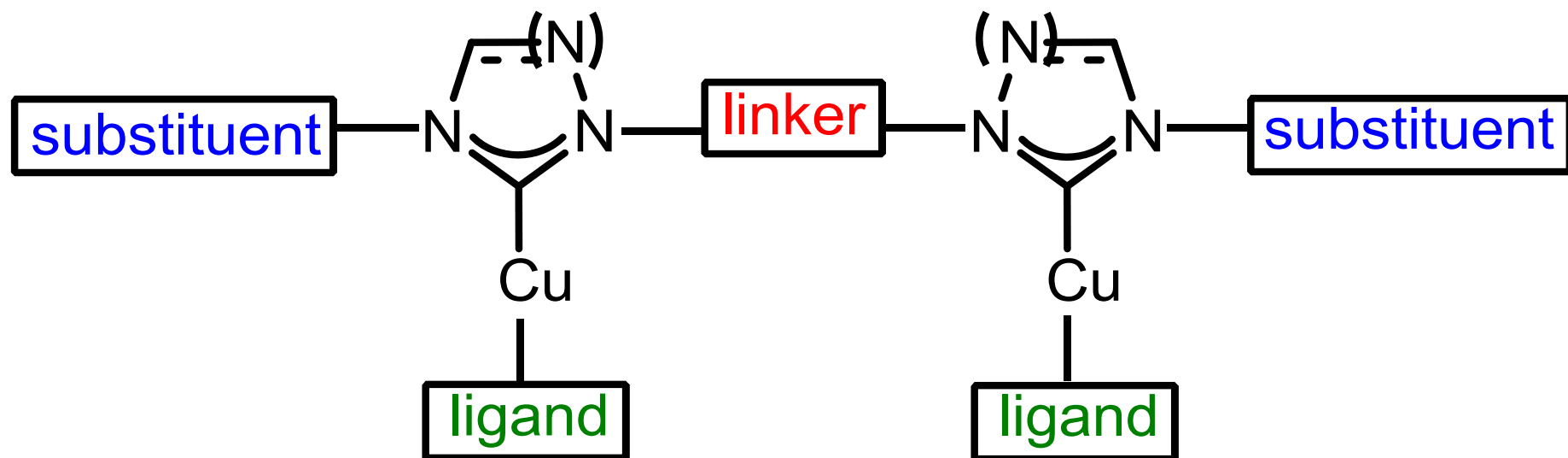


Christoph Nolte, Peter Mayer, Bernd F. Straub*,
Angew. Chem. **2007**, *119*, 2147-2149;
Angew. Chem. Int. Ed. **2007**, *46*, 2101-2103

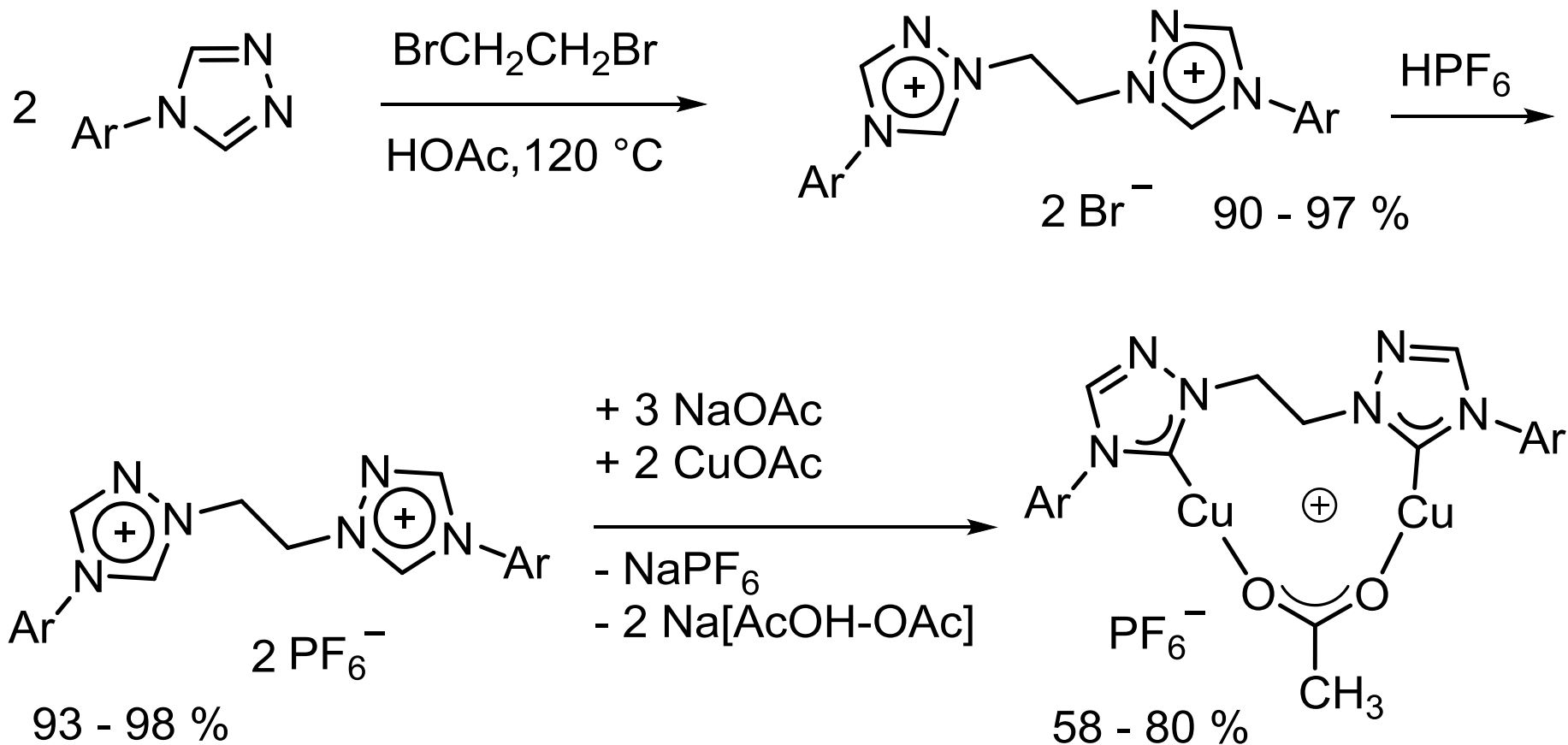
Mechanistic Conclusion



Catalyst Design: Irreversible Coordination of Two Copper(I)

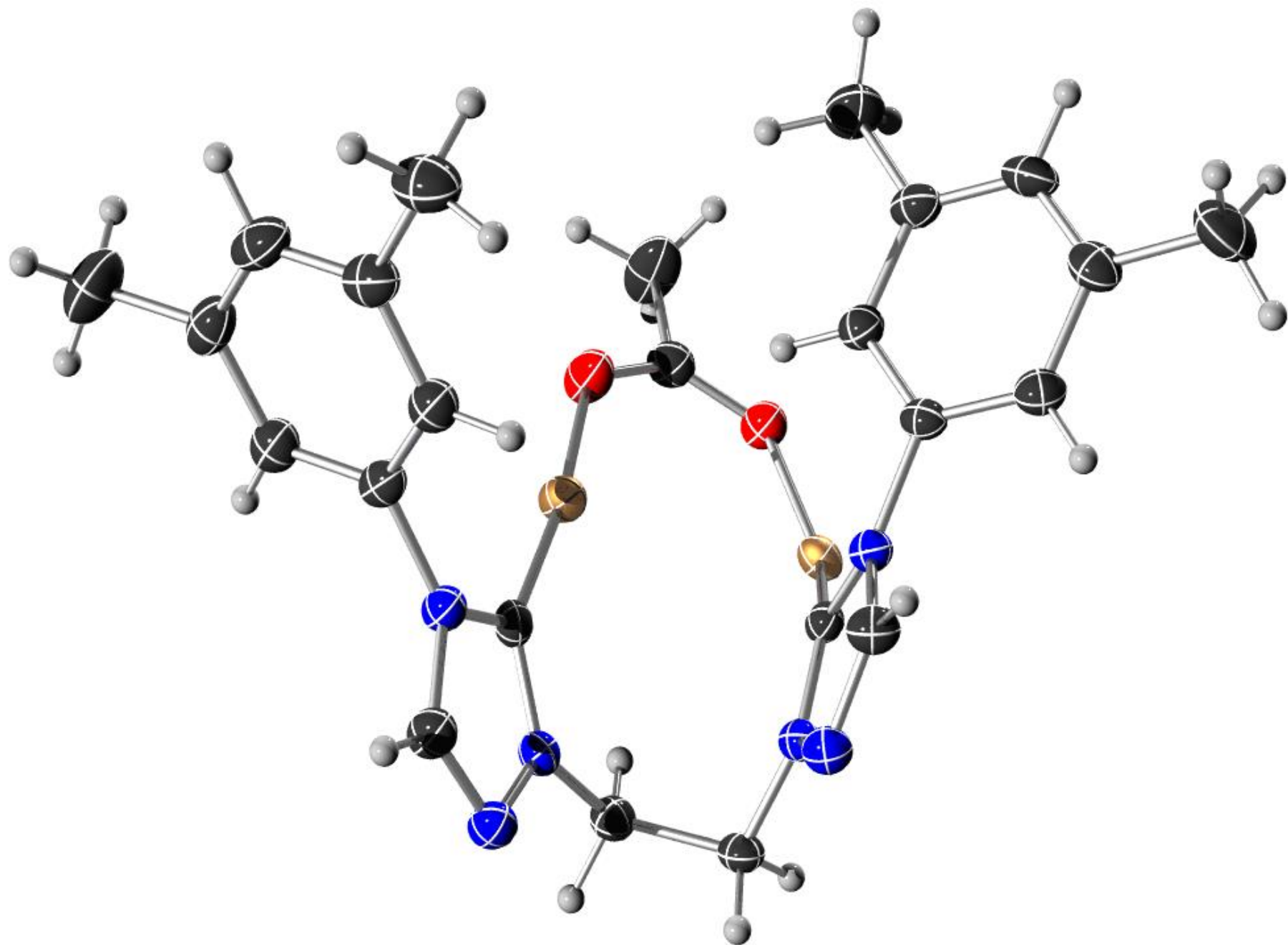


Acetate as Sacrificial Ligand

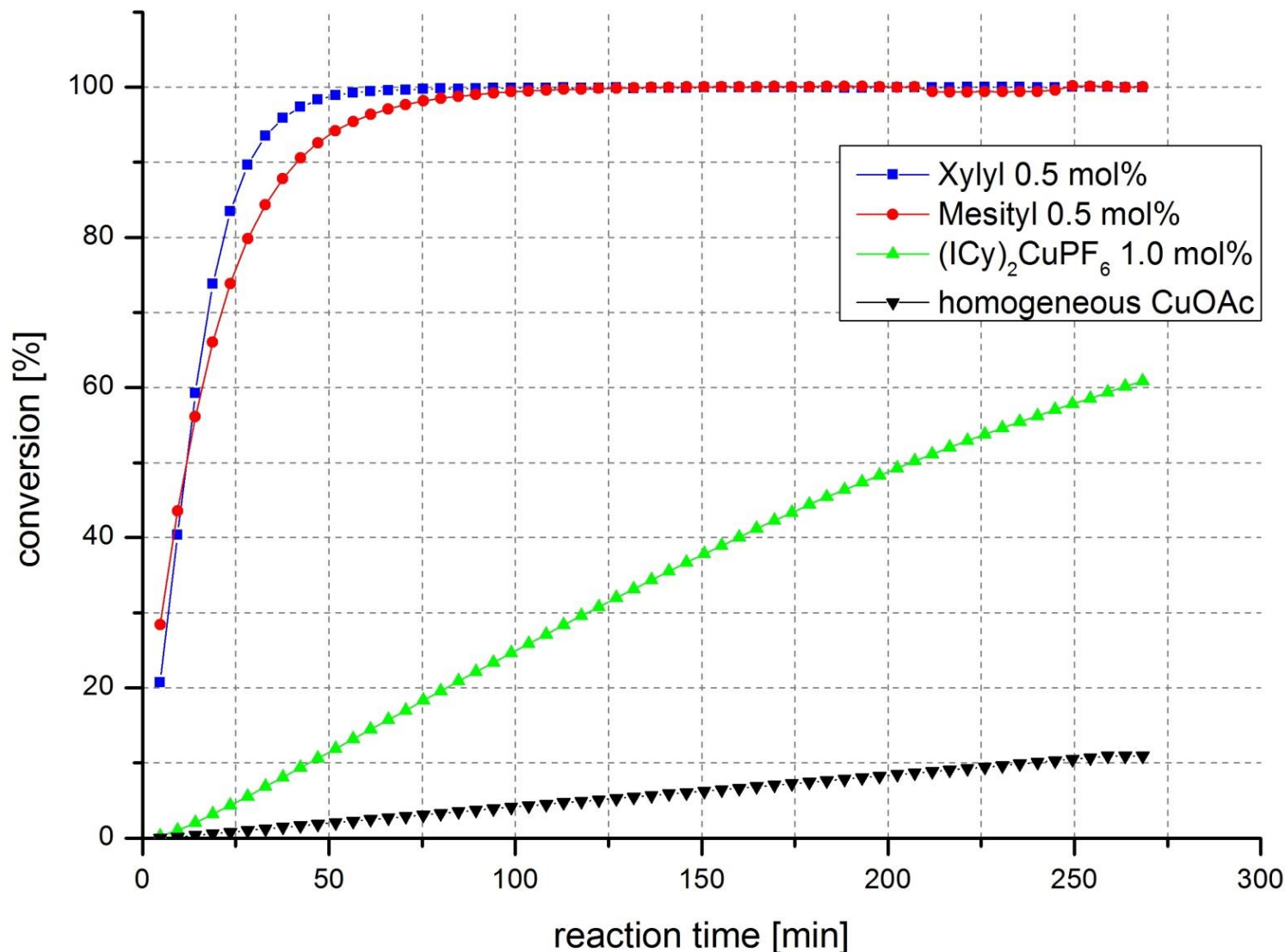


Regina Berg, Johannes Straub, Ella Schreiner, Steffen Mader, Frank Rominger, Bernd F. Straub*, *Adv. Synth. Catal.* **2012**, 354, 3445-3450.

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



Homogeneous CuAAC Catalysis



296 K,
CD₂Cl₂
0.6 M PhCCH
0.6 M BnN₃