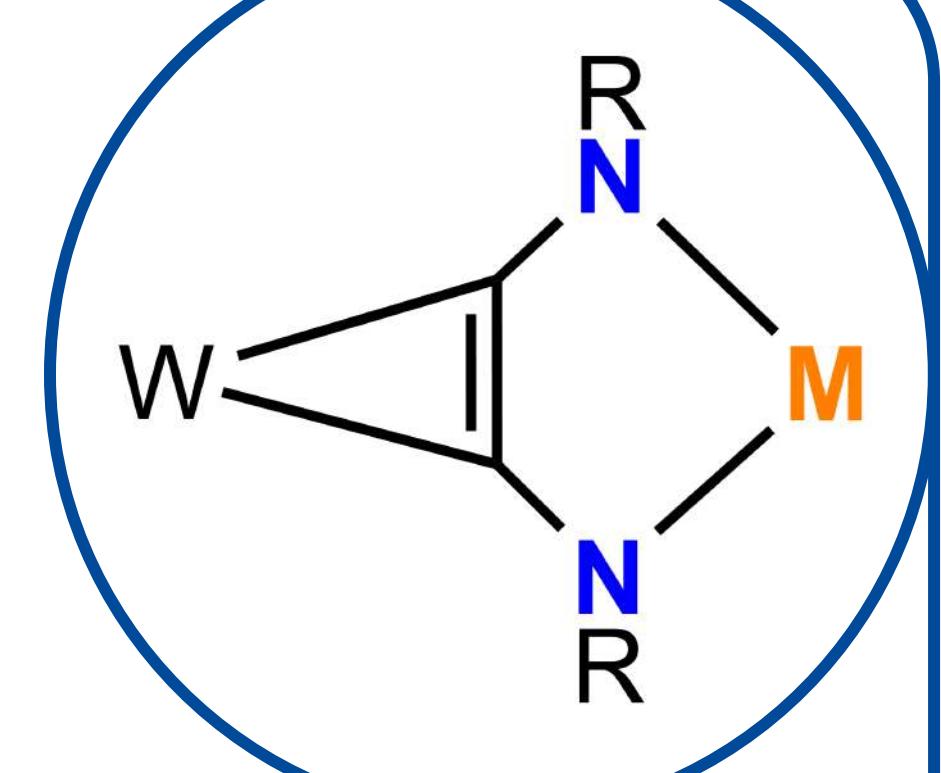
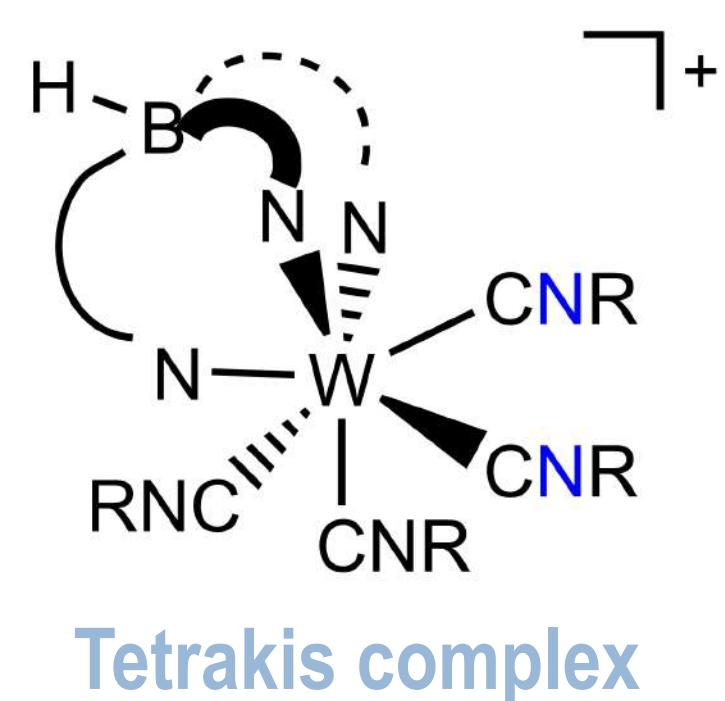
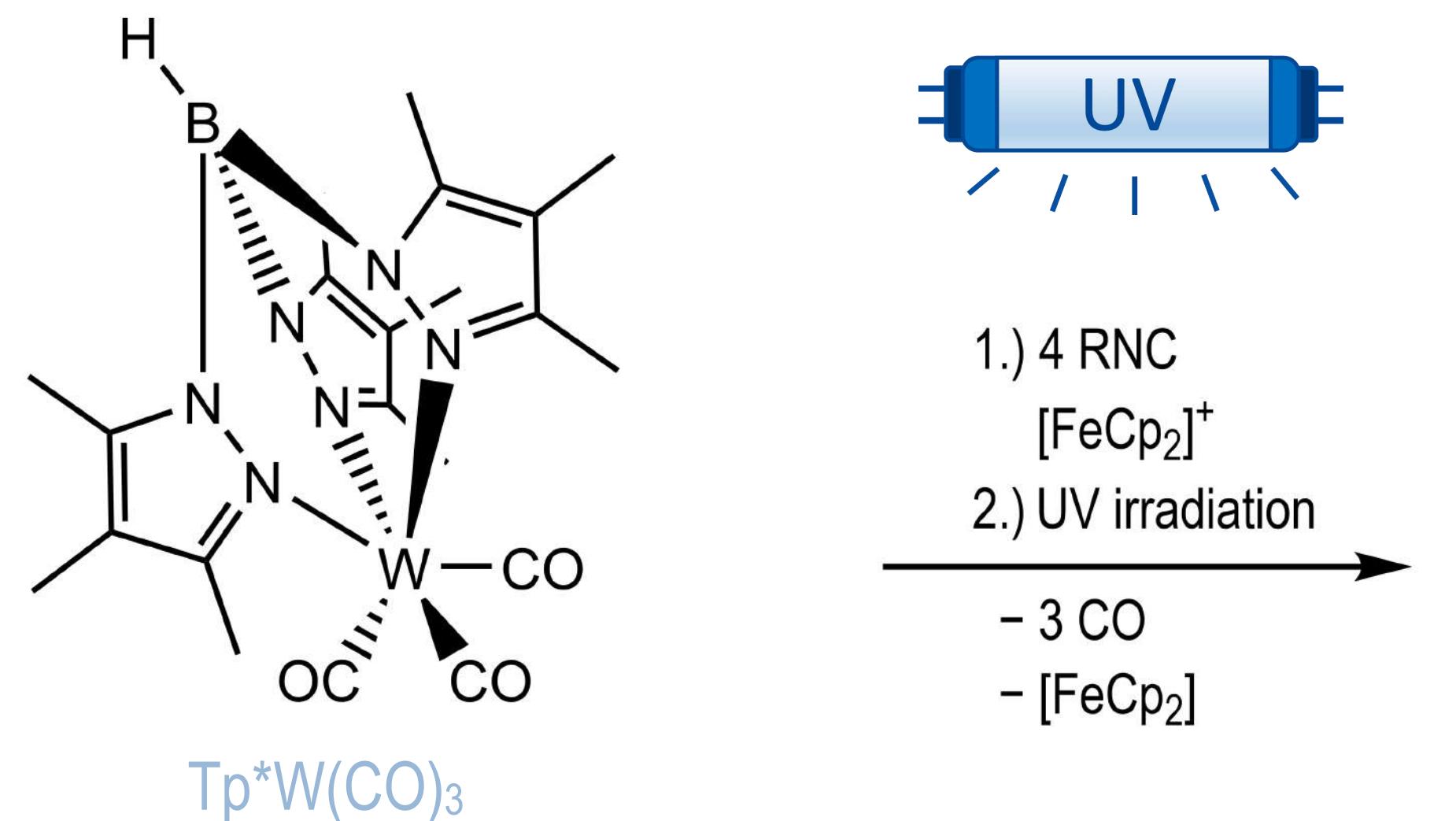


Synthesis and Characterization of Polynuclear Metalla-Ketiminate Complexes

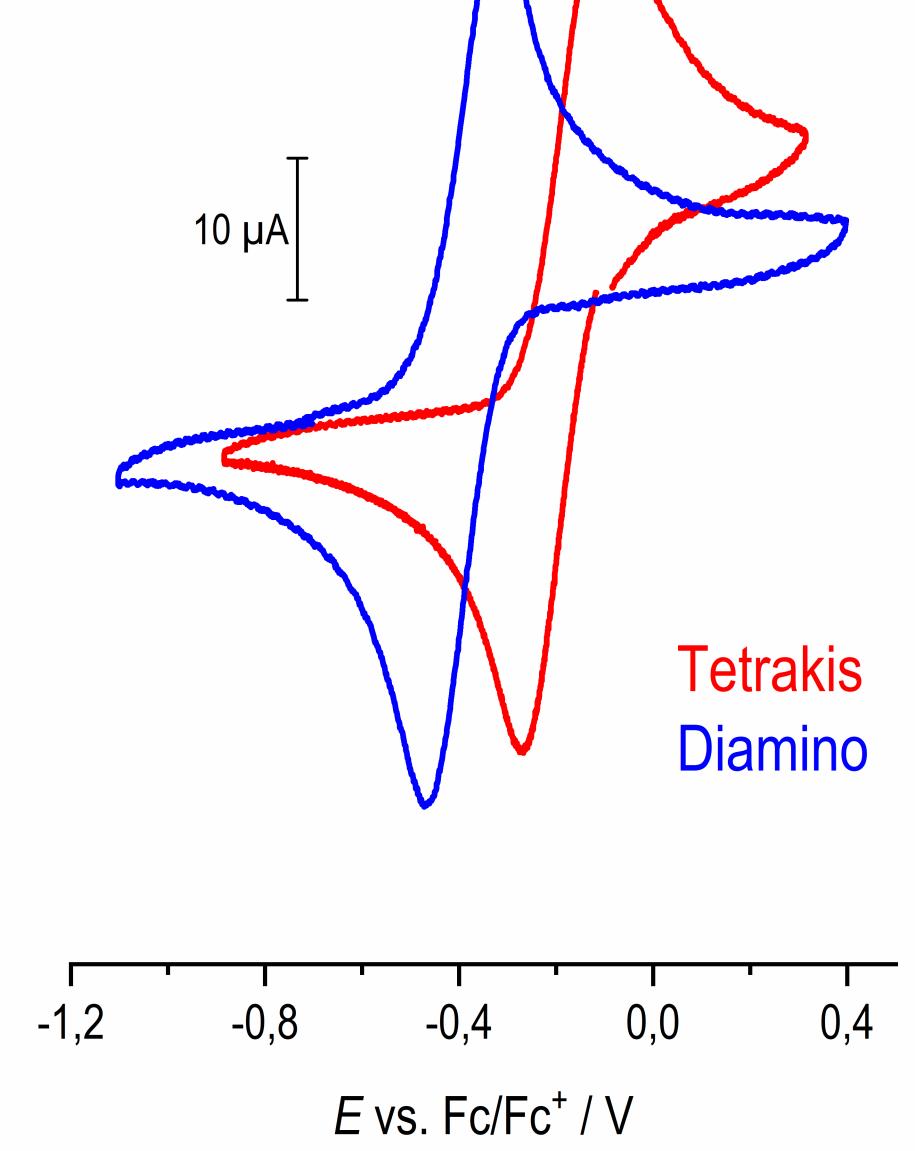
Malte-Joseph B. Reihwald, Christopher Timmermann, Alexander Villinger, Florian Taube and Wolfram W. Seidel*



Introduction



The direct use of alkynes with secondary amine substitution is impossible because of an intrinsic instability due to the proton migration along the alkyne triple bond (see above). So the alkyne is formed by coordination of four isonitrile ligands (under UV irradiation) and subsequent reductive coupling of two ligands with zinc in ethanol.^[1]



But is the coupling truly reductive?
Let's have a look at the $\text{W}^{II}/\text{W}^{III}$ oxidation process in the CV spectrum ($R = t\text{-Bu}$):

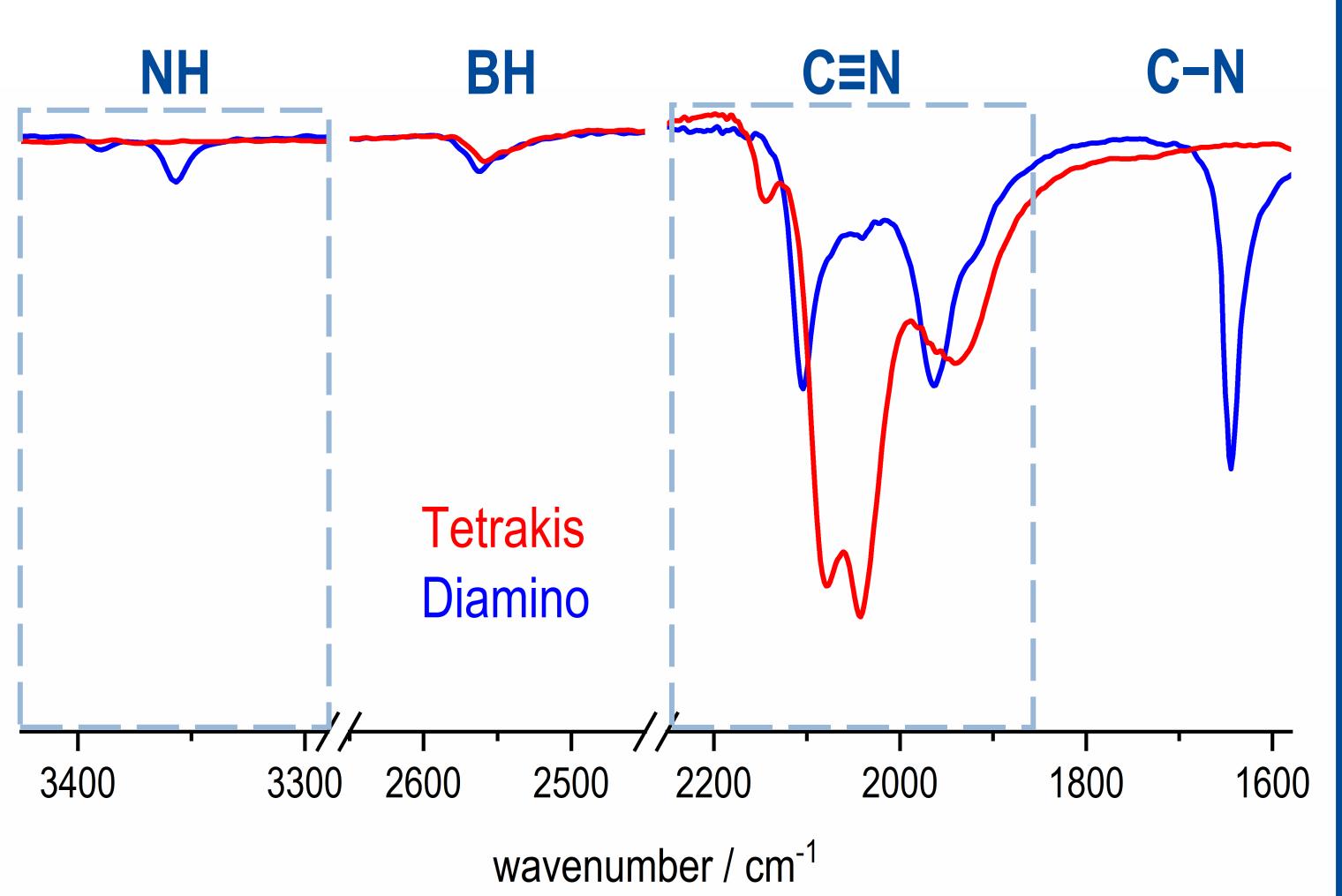
Before: -130 mV
After: -390 mV

Yes, there is increased electron density at the W-center after the coupling.

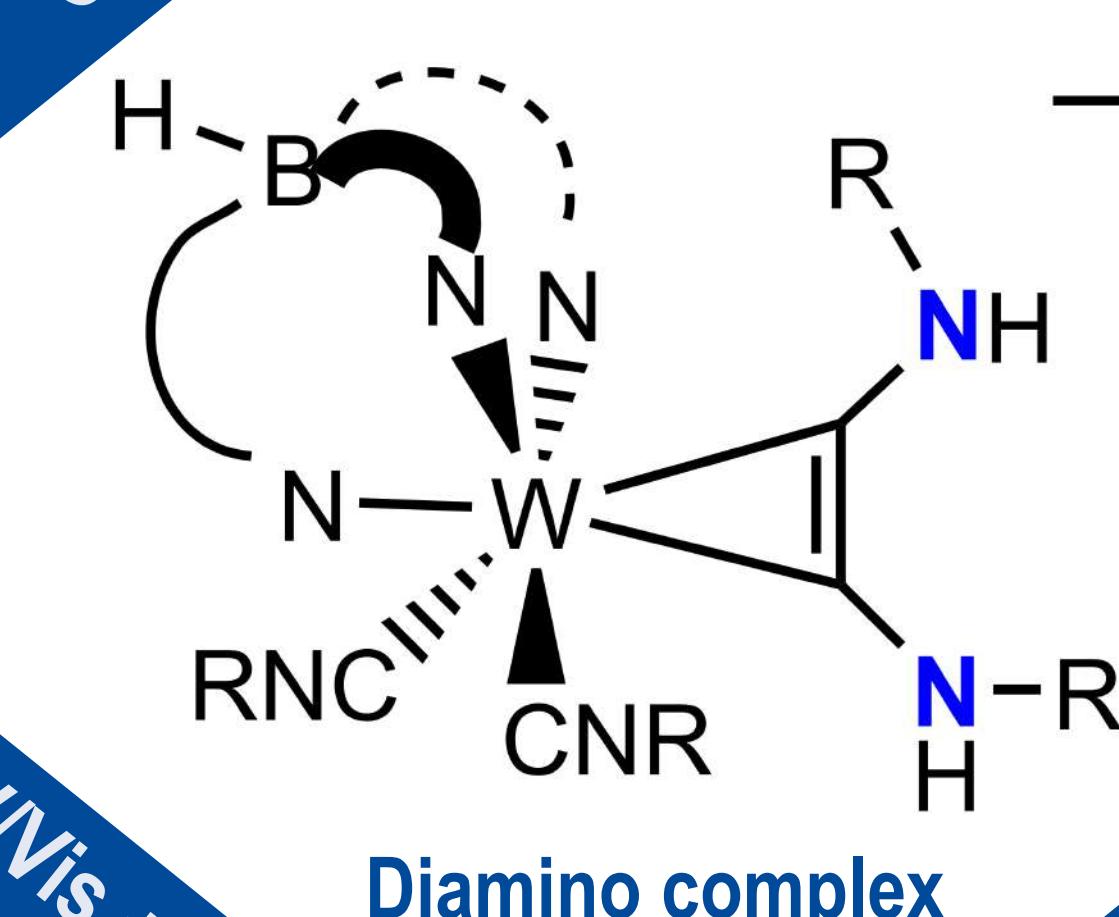
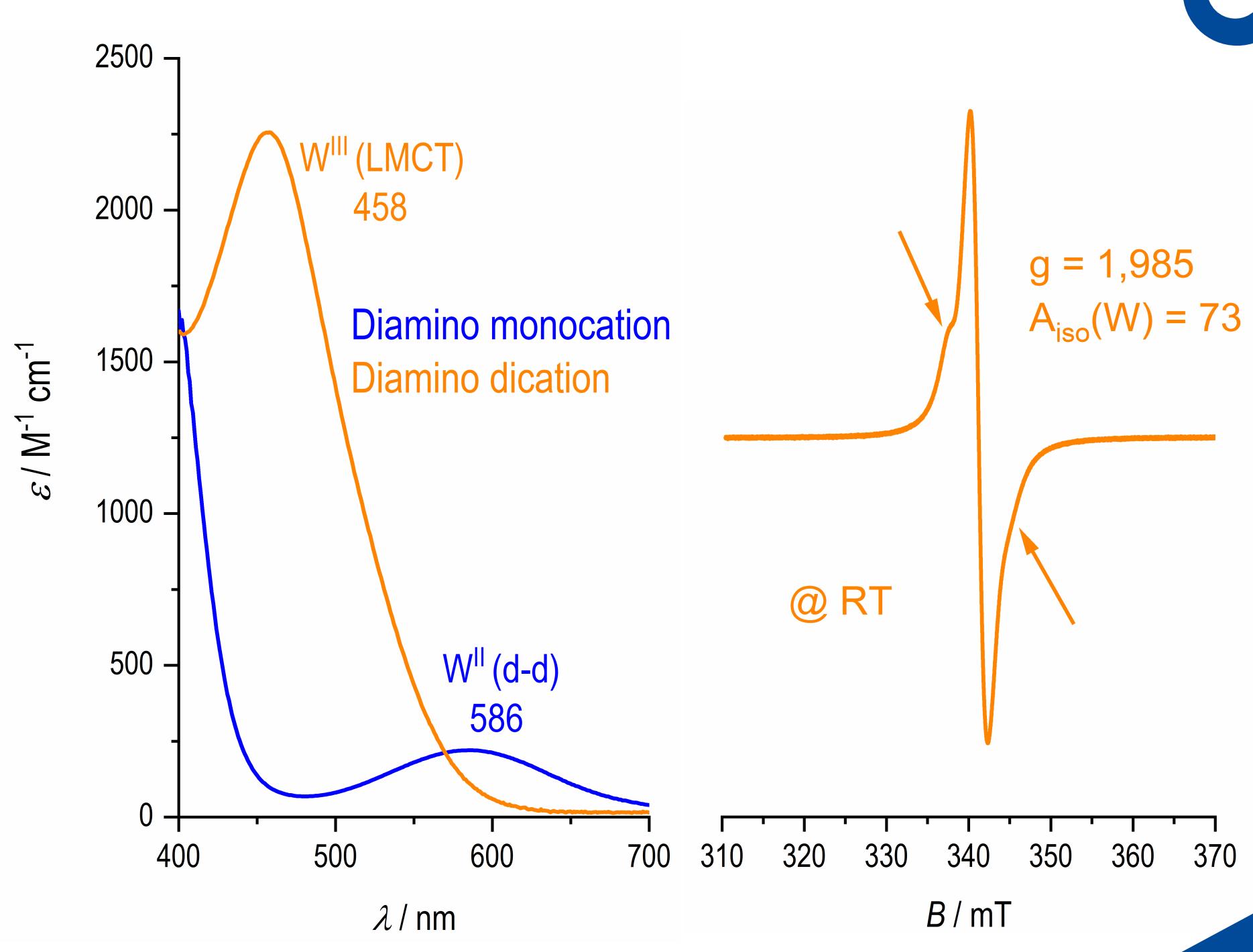
Reductive Coupling



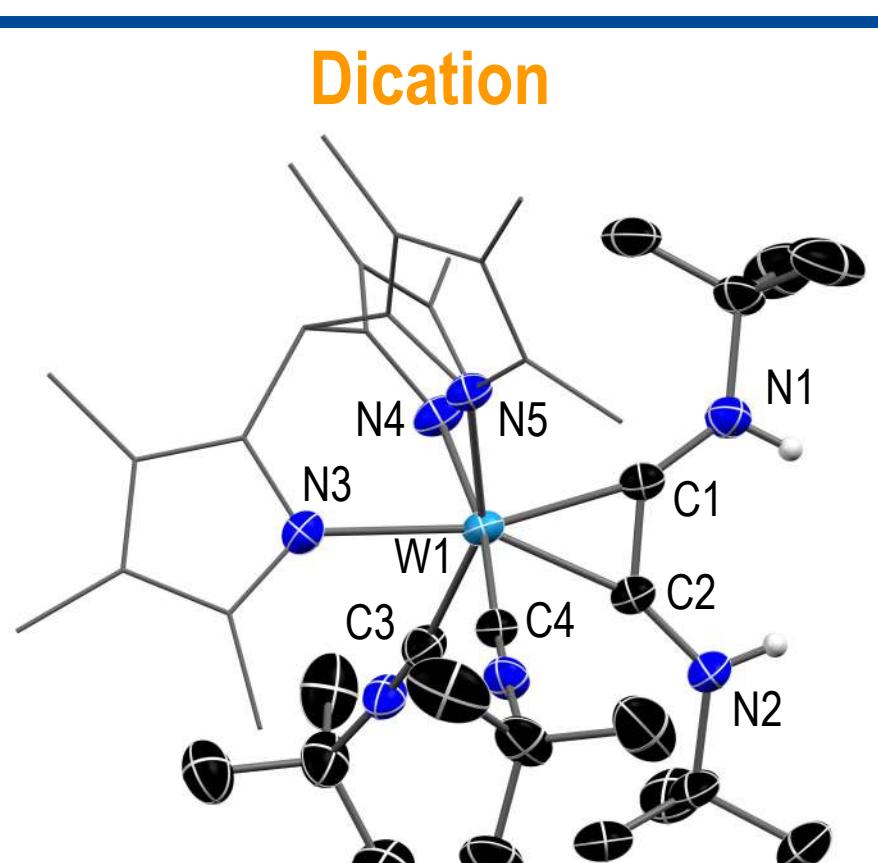
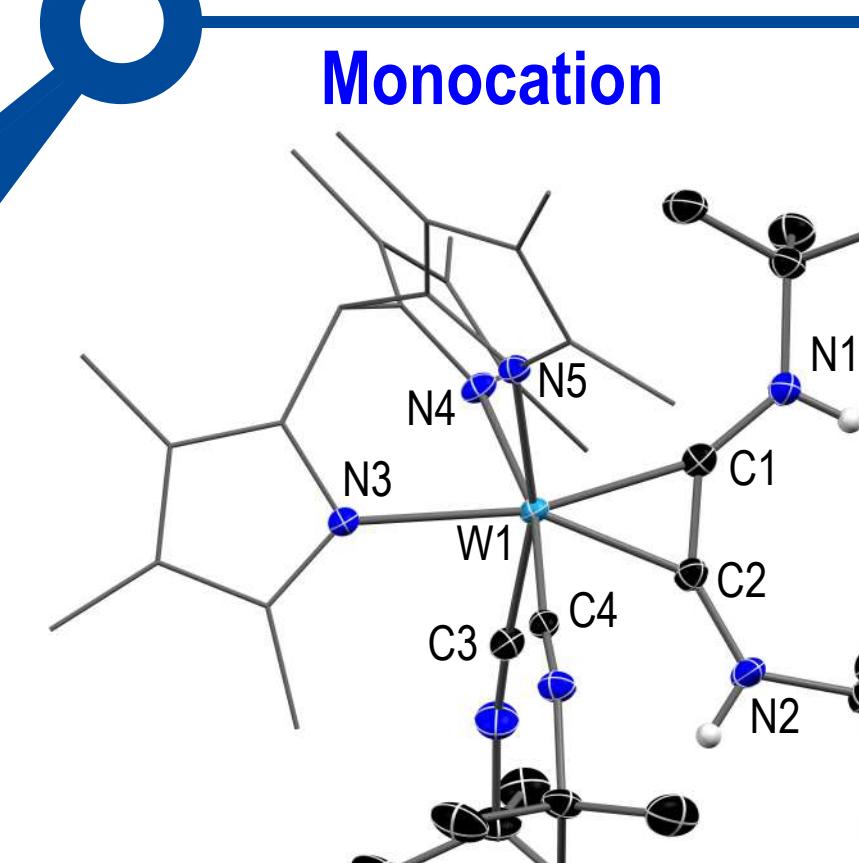
	Tetrakis	Diamino
NH	-	3390, 3357
BH	2559	2561
C≡N	2145, 2079, 2042, 1941	2104, 2040, 1964
C-N	-	1644



After the reductive coupling, the ATR-IR spectrum shows stretching bonds for the new NH and CN vibrations of the diamino complex ($R = t\text{-Bu}$).



X-Ray



W1-N3: 2,273(1)
W1-N4: 2,207(2)
W1-N5: 2,195(1)
W1-C1: 2,074(2)
W1-C2: 2,027(2)

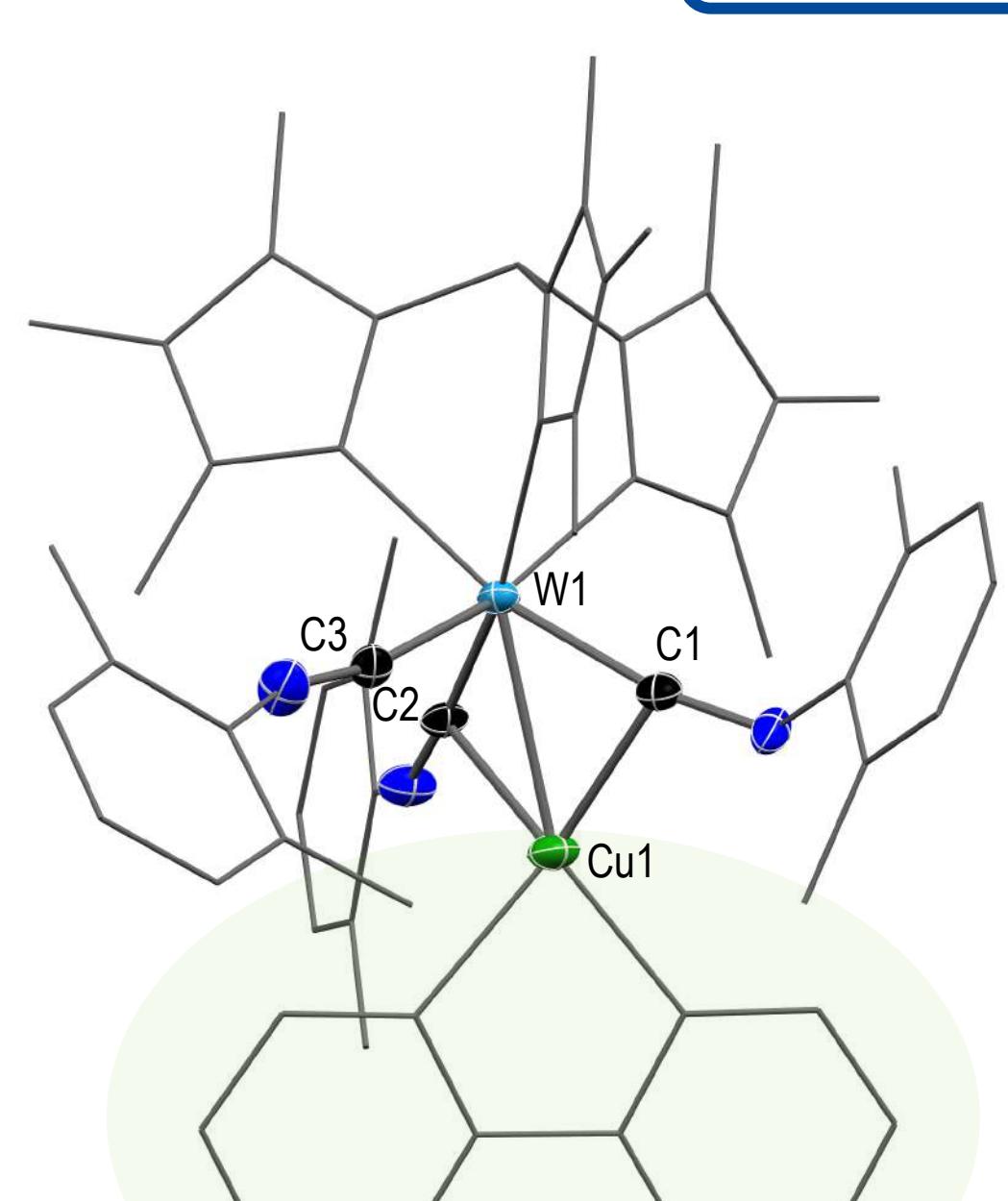
2,223(2)
2,154(2)
2,162(2)
2,136(3)
2,127(3)

bond lengths / Å

Deprotonation



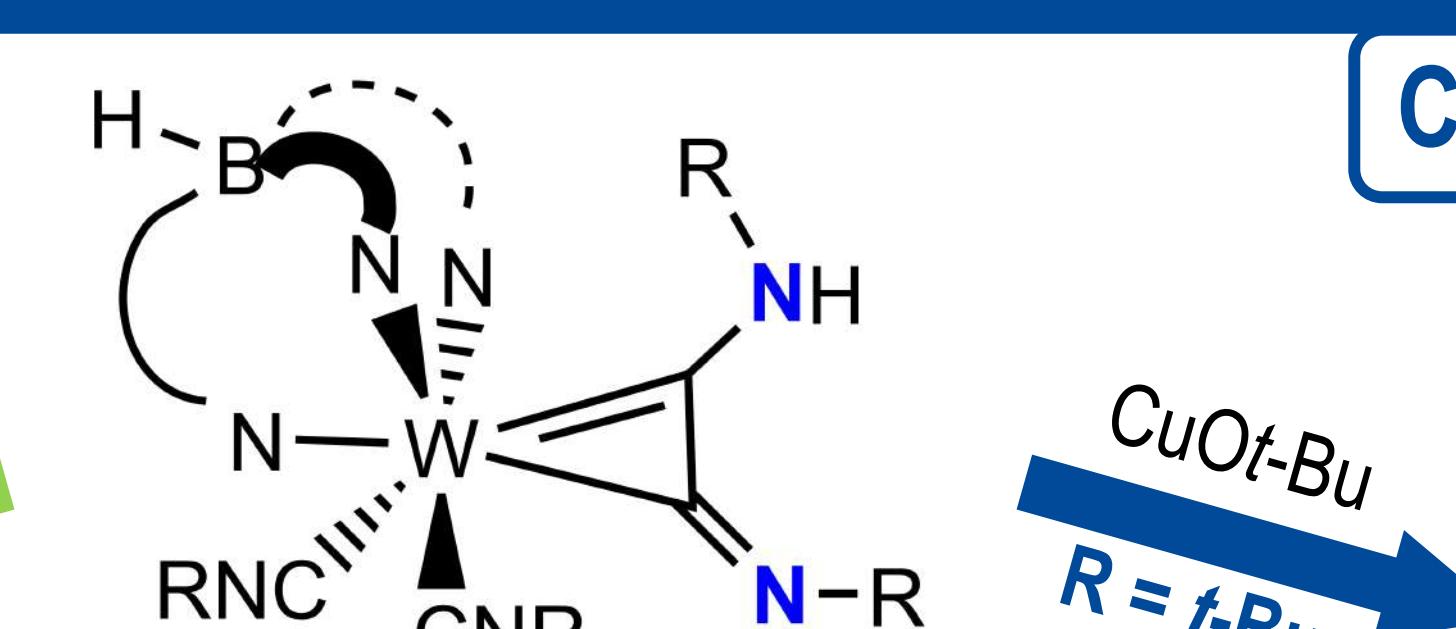
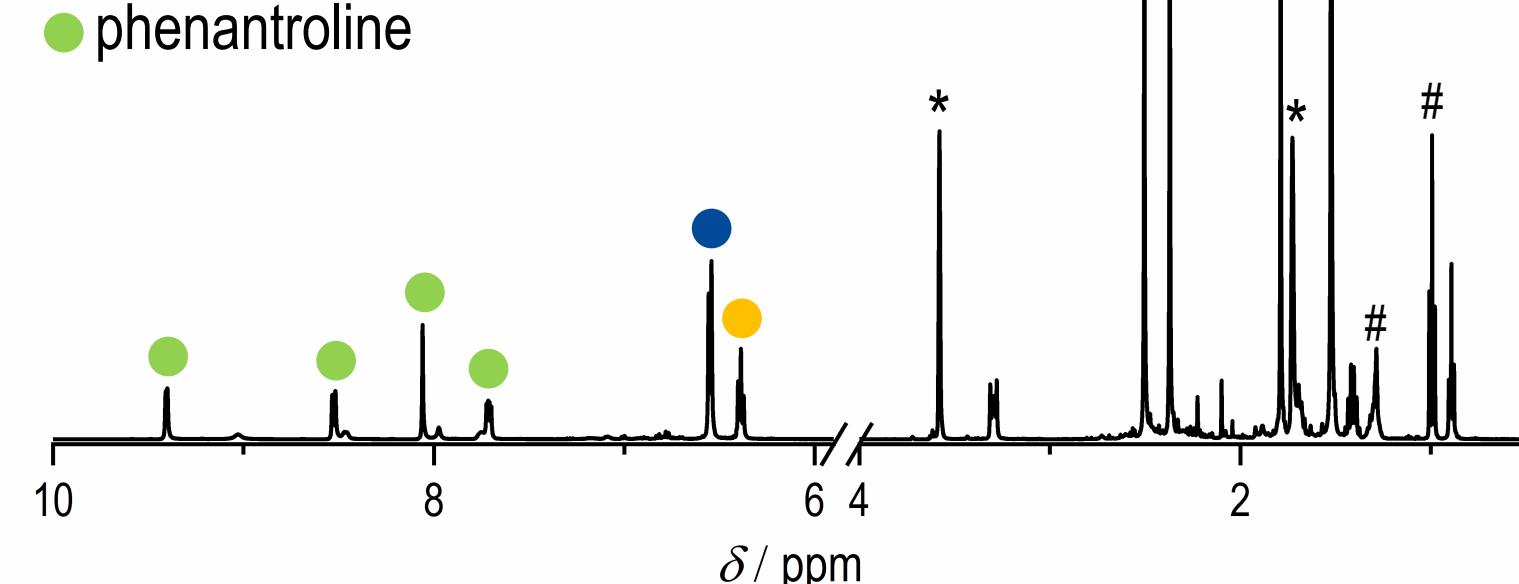
Polynuclear Complexes



In the solid state, two isonitriles bridge the $\text{W}-\text{Cu}$ bond, but in solution we observe C3-symmetry in the $^1\text{H-NMR}$ with three Tp^* -signals and only one set of signals for the xyl protons.

W1-C1	1,990(2) Å
W1-C2	1,9692) Å
W1-C3	1,964(4) Å
W1-Cu1	1,990(2) Å
Cu1-C1	2,211(2) Å
Cu1-C2	2,056(2) Å
Cu1-C3	2,934(6) Å

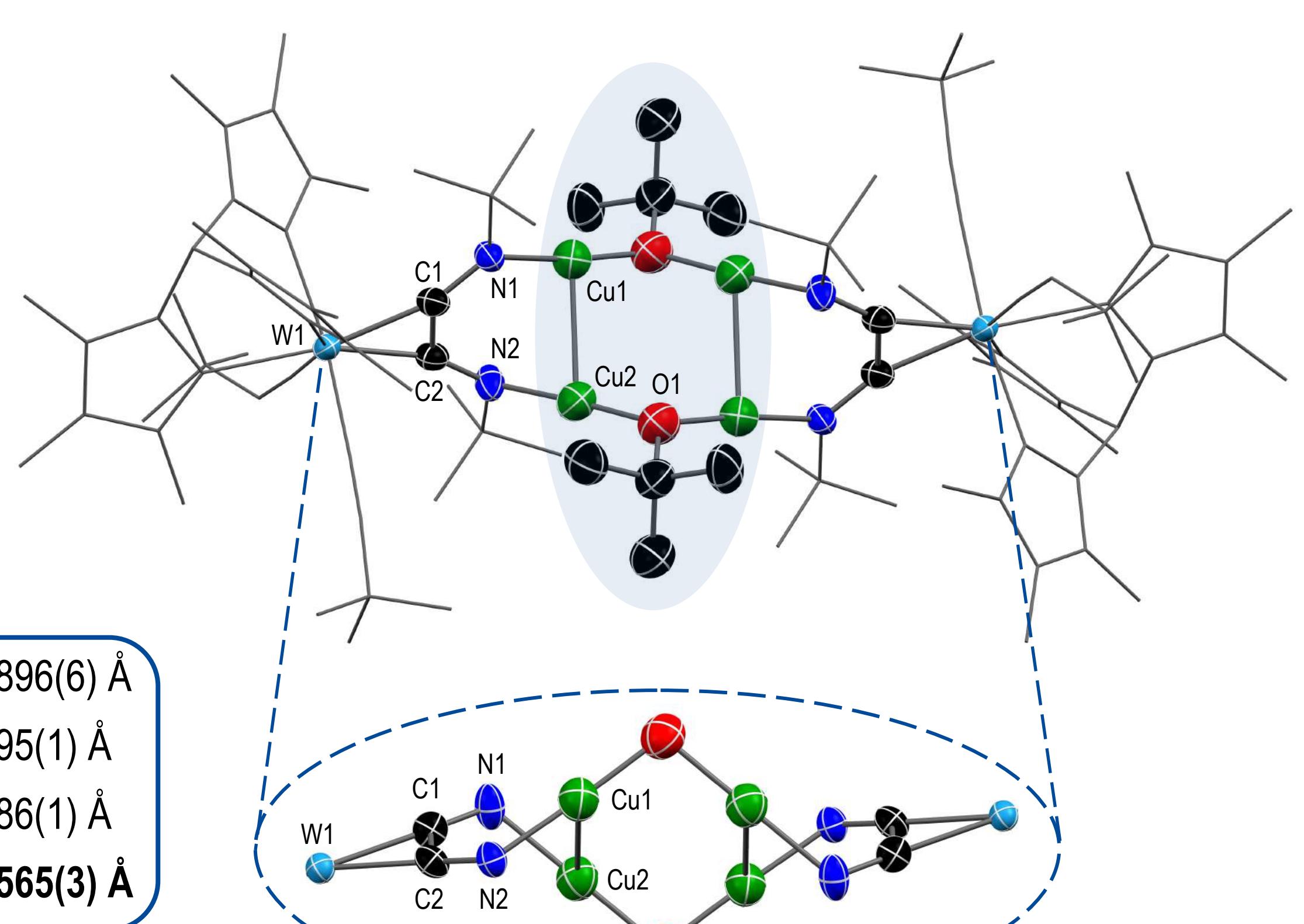
- * THF-d₈
- # Pentane
- $\text{Tp}^*\text{-CH}_3$
- Xy-CH_3
- $\text{Xy-H}_{\text{para}}$
- $\text{Xy-H}_{\text{meta}}$
- phenanthroline



Coordination via N-donors

Addition of 2 eq. Cu^{i} $t\text{-butoxide}$ does not result in an chelate complex. The result of a XRD analysis reveals four copper and two tungsten centers, in which each Cu-centre is bonded to one nitrogen, one copper and one oxygen atom of the $t\text{-butoxide}$.

N1-Cu1 1,896(6) Å
N2-Cu2 1,95(1) Å
Cu2-O1 1,86(1) Å
Cu1-Cu2 2,565(3) Å



[1] a) C. T. Lam, M. Novotny, D. L. Lewis, S. J. Lippard, *Inorg. Chem.* 1978, 17, 2127–2133; b) J. C. Dewan, C. M. Giandomenico, S. J. Lippard, *Inorg. Chem.* 1981, 20, 4069–4074; c) F. A. Cotton, S. A. Duraj, W. J. Roth, *J. Am. Chem. Soc.* 1984, 106, 6987–6993; d) A. C. Filippou, W. Grünleitner, C. Völk, K. Kiprof, *Angew. Chem. Int. Ed.* 1991, 30, 1167–1169.