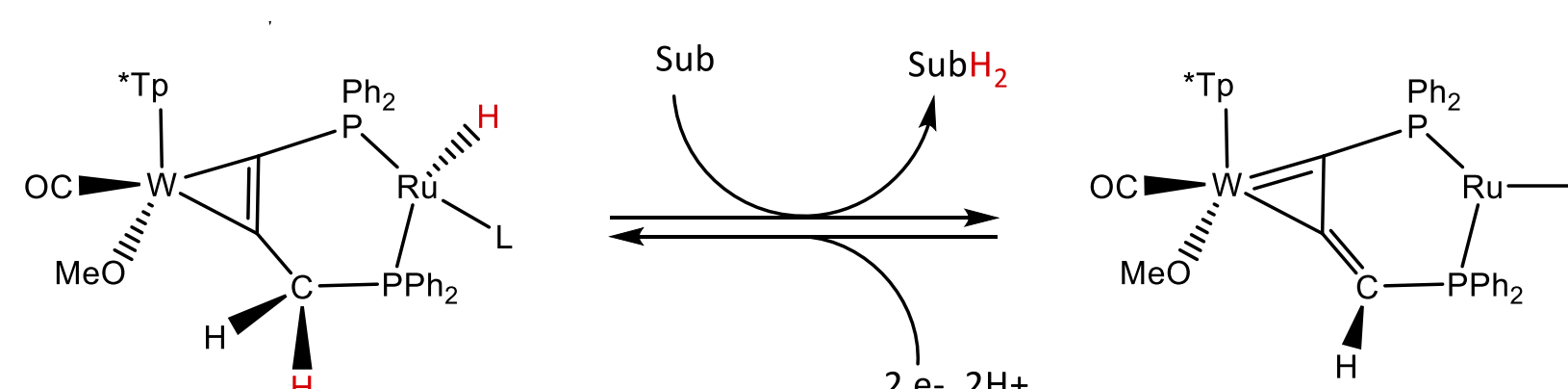


# Heterobimetallic Mediators for Electrocatalytical Hydrogenation

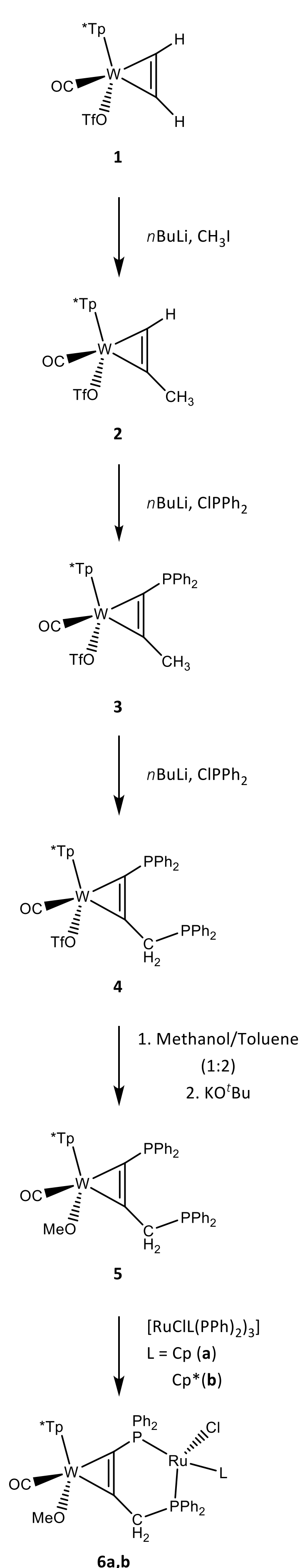
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## Motivation

Air stable heterobimetallic W/Ru complexes, in which the metals are linked by an acetylene-diphosphine bridging ligand, have previously been shown to be applicable as catalysts providing a potentially redox-active alkyne complex backbone.[1] In subsequent studies, a novel ligand on this base bearing a methylene spacer was developed. The protic hydrogen at the propargylic position and a hydride at the metal are perfectly suited for polar hydrogen transfer, making these complexes promising candidates for application in indirect electrocatalysed hydrogenation. This approach can offer the advantage of milder conditions and eliminate the need for high pressures.

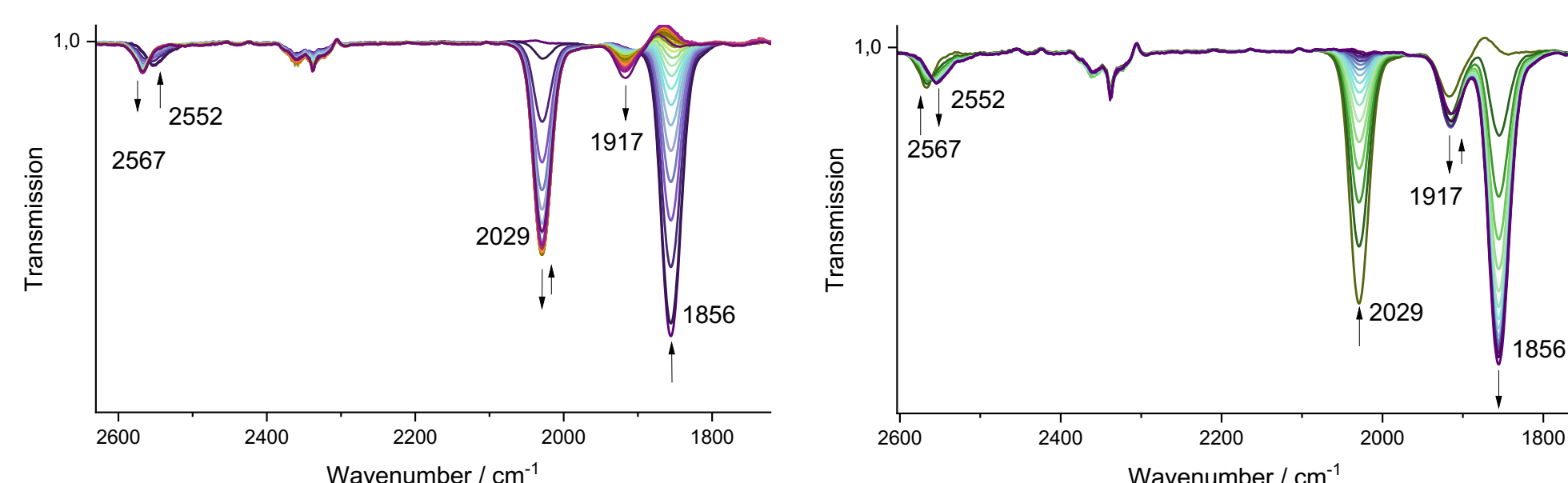


## Synthetic Approach

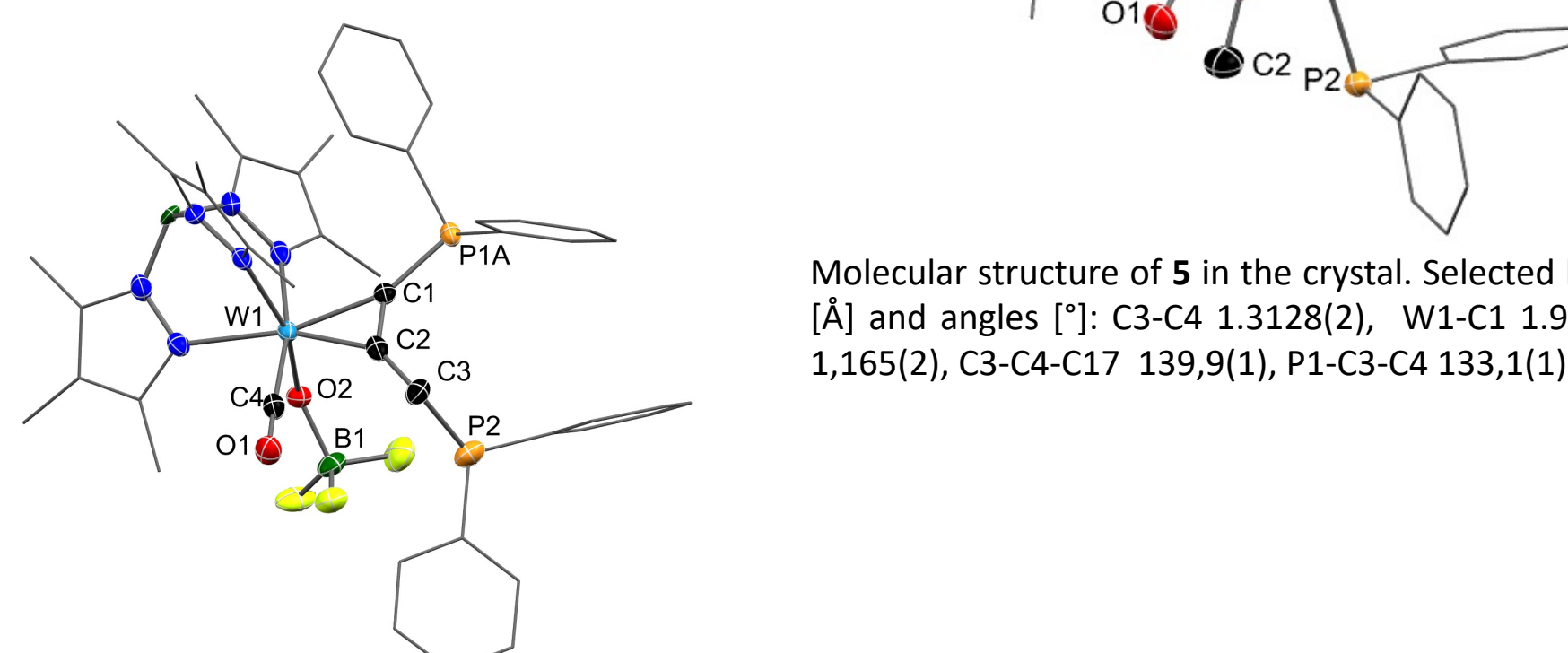


## Introducing an Alcoholate Ligand

The synthesis of compounds **1–4** could be realised by firstly introducing a methyl-group at the side-on coordinated alkyne, then adding phosphine groups in two consecutive steps. The deliberate introduction of an alcoholate-ligand at the tungsten-centre was achieved by treating **4** with a solvent-mixture of methanol and toluene under reflux. Thus, complex **5** could be obtained, which shows interesting behaviour in spectro-electro-chemical measurements that points to the formation of an unexpected side-product. When oxidizing **5** chemically compound **8** was formed, which shows the formation of a dianionic borate-ligand in place of the alcoholate.



IR-SEC-Measurement of **5** for oxidation at a static potential of 300 mV (left) and subsequent reduction at a static potential of 0 V (right). Measured in dichloroethane, c(**5**) = 6 mmol/l, c(NBu<sub>4</sub>PF<sub>6</sub>) = 0,26 mol/l.



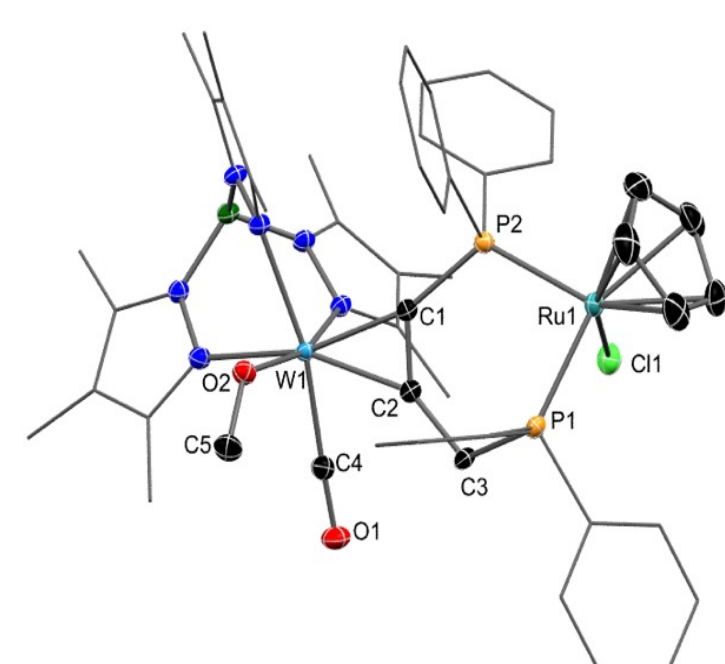
Molecular structure of **5** in the crystal. Selected bond lengths [Å] and angles [°]: C3-C4 1.3128(2), W1-C1 1.932(2), C1-O1 1.165(2), C3-C4-C17 139,9(1), P1-C3-C4 133,1(1).

Molecular structure of **8**(BF<sub>4</sub>) in the crystal. Selected bond lengths [Å] and angles [°]: C1-C2 1,312(8), W1-C4 1,958(6), C4-O1 1,151(8), C1-C2-C3 139,2(6), P1A-C3-C4 139,2(6).

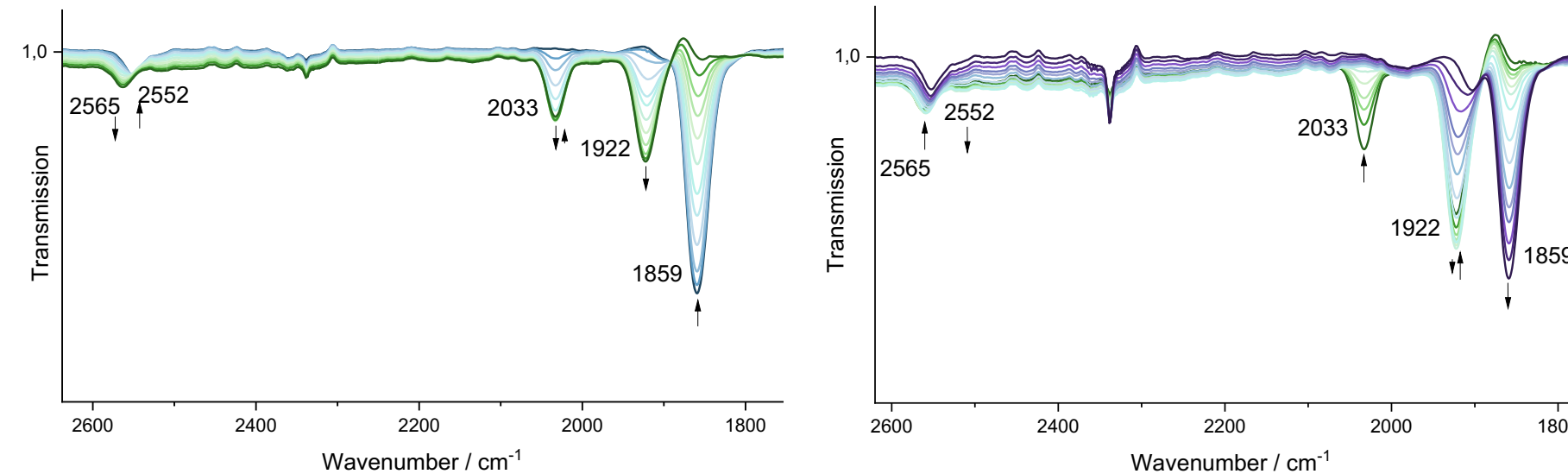
## Synthesis of Heterobimetallic Complexes

The compounds **6a** and **6b** were synthesized from **5** using [RuCl(PPh<sub>3</sub>)<sub>2</sub>] (L = Cp (**a**), Cp\* (**b**)). For both compounds the molecular structure could be determined by X-ray analysis. The cyclic voltammograms of these compounds show two reversible oxidations which can be assigned to W(II)/(III) for the lower and Ru(II)/(III) for the higher potential. Complex **6a** shows a similar behaviour to **5** in the IR-SEC-measurements, however the formation of a related side-product here is fully reversible.

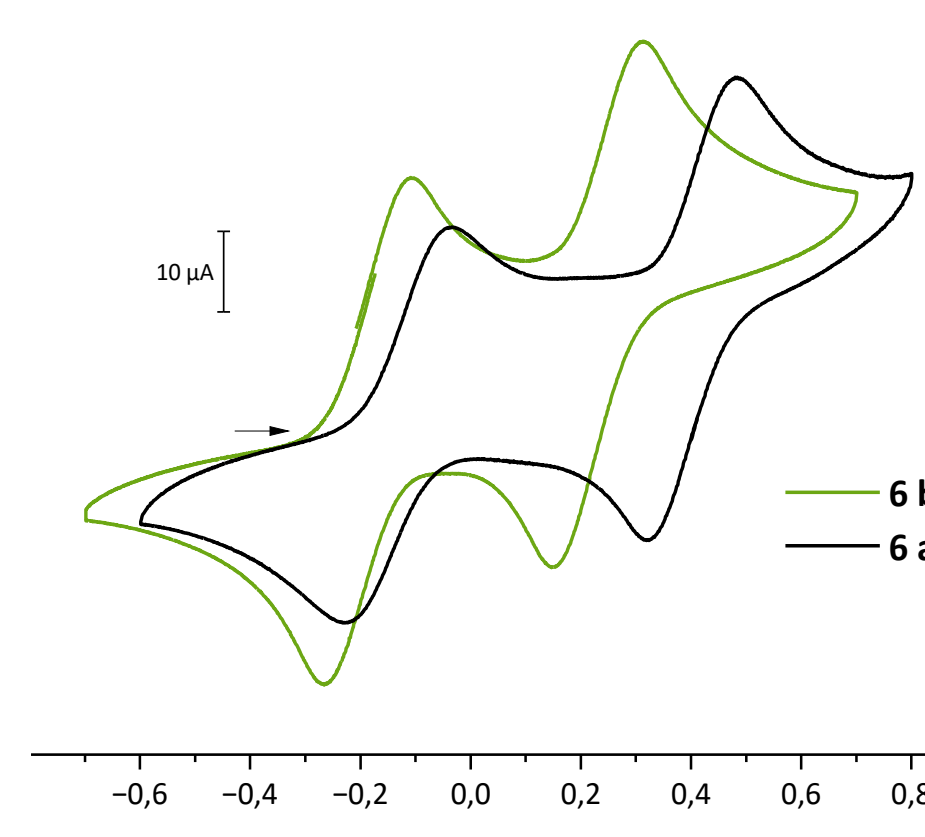
| compound  | E <sub>1/2</sub> of W(II)/(III) / mV | E <sub>1/2</sub> of Ru(II)/(III) / mV |
|-----------|--------------------------------------|---------------------------------------|
| <b>6a</b> | -290                                 | 250                                   |
| <b>6b</b> | -340                                 | -80                                   |



Molecular structure of **6a** in the crystal. Selected bond lengths [Å] and angles [°]: C1-C2 1.318(3), W1-C4 1.943(2), C4-O1 1.175(3), C1-C2-C3 137,7(2), C2-C3-P1 112,4(1), P2-C1-C2 125,5(1), P2-Ru1-P1 91,20(2).



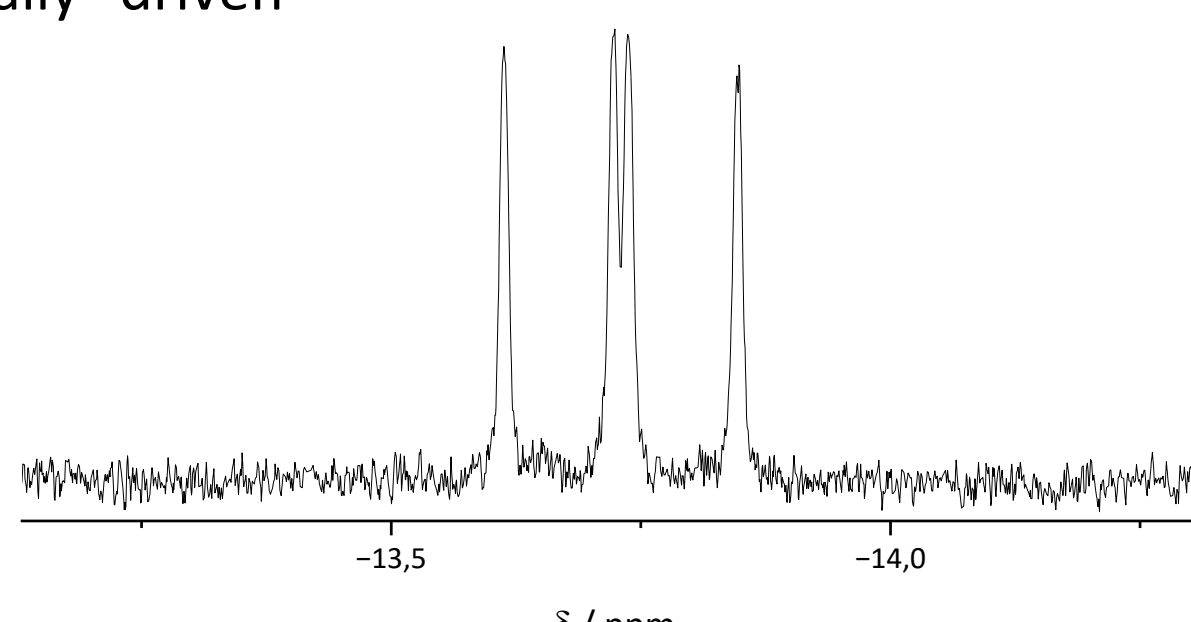
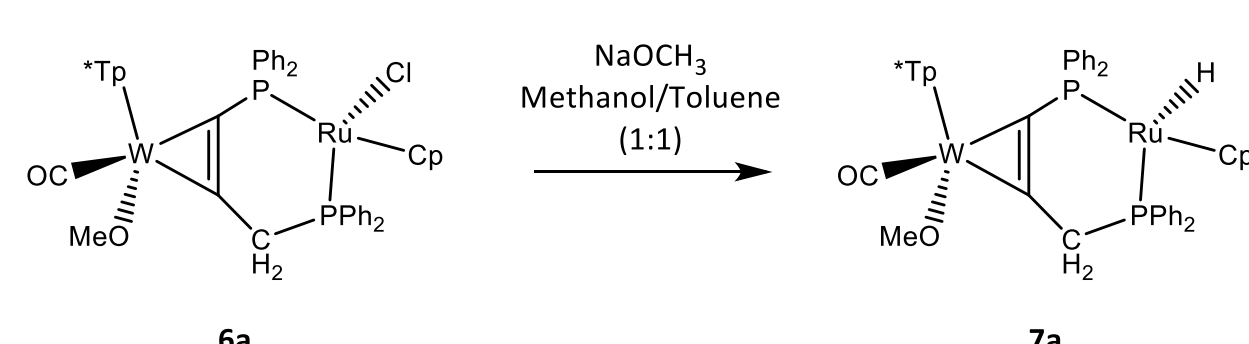
IR-SEC-Measurement of **6a** for oxidation (left) and subsequent reduction (right). Measured in dichloroethane, c(**6a**) = 6 mmol/l, c(NBu<sub>4</sub>PF<sub>6</sub>) = 0,26 mol/l.



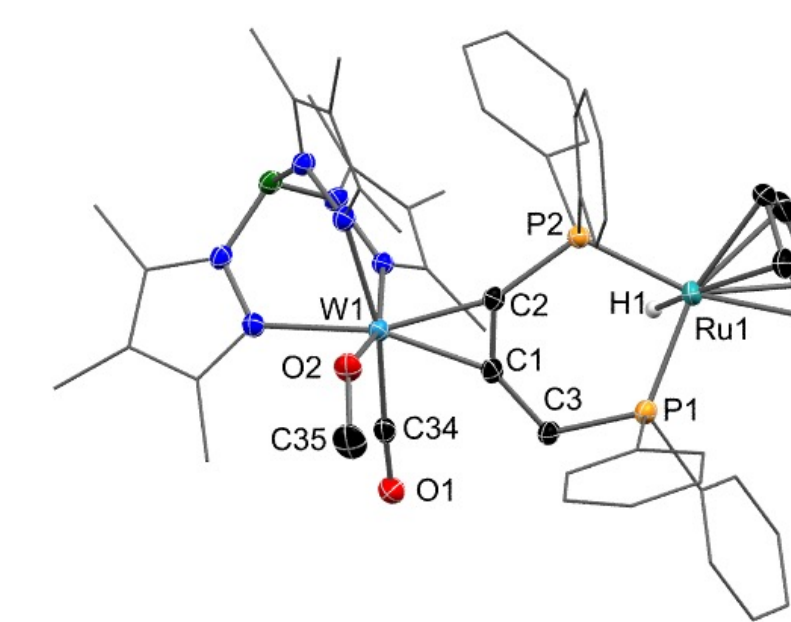
Cyclic Voltammograms of **6a** and **6b** in dichloromethane. (0.10 M n-Bu<sub>4</sub>NPF<sub>6</sub>, 100 mV/s, vs Fc/Fc<sup>+</sup>).

## Synthesis of a Ru-Hydride-Complex

By treating **6a** with NaOCH<sub>3</sub> under reflux the chloride-ligand at the Ru-centre was substituted for a hydride leading to the desired complex **7a**. This complex bearing the methylene spacer as well as a hydride in close proximity is now suited for further investigations targeting the use of **7a** as a mediator for electrochemically driven hydrogenation reactions.



Hydride-signal of **7a** in the <sup>1</sup>H NMR spectrum (measured in CDCl<sub>3</sub>).



Molecular structure of **6b** in the crystal. Selected bond lengths [Å] and angles [°]: C1-C2 1.312(3), W1-C4 1.937(3), C34-O1 1.174(3), C2-C1-C3 137,8(2), C1-C3-P1 111,2(2), P2-C2-C1 125,9(2), P1-Ru1-P2 92,83(3).