

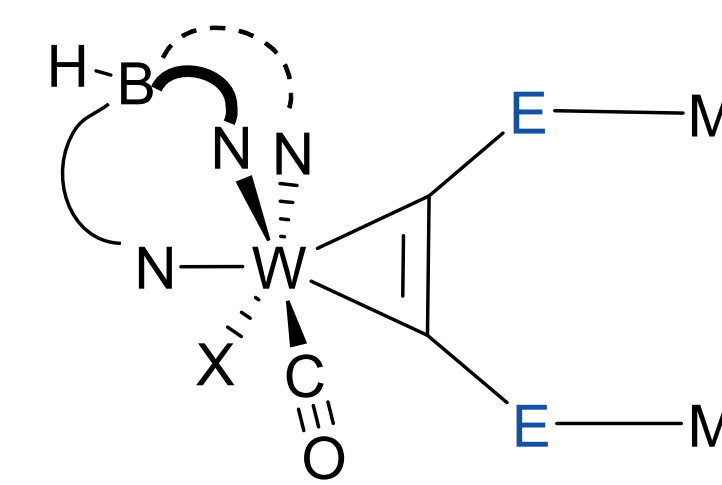
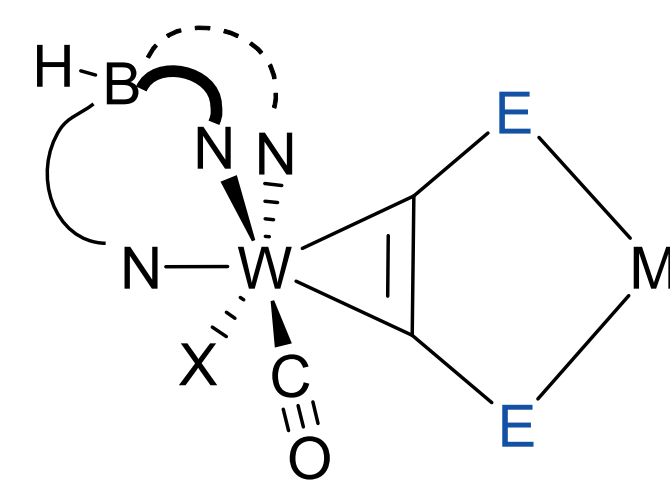
# SYNTHESIS AND COORDINATION CHEMISTRY OF NEW $\alpha$ -SILICON ALKYNE COMPLEXES

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CONCEPT

The Seidel group investigates  $\alpha$ -donor substituted alkynes as valuable bridging unit between two metals in the  $\mu$ - $\eta^2$ -C,C'- $\kappa^2$ -E,E'-binding mode. This system proves to be very versatile, as a great variation of donor atoms (C, N, O, P, S) could be introduced in various symmetric and asymmetric combinations, leading to a wide range of polynuclear complexes, that show strong electronic cooperativity of the metal centres. [1-5]

E	C	N	O	P	S
C	✓	✓		✓	
N	✓				✓
O				✓	✓
P	✓			✓	✓
S		✓	✓	✓	✓

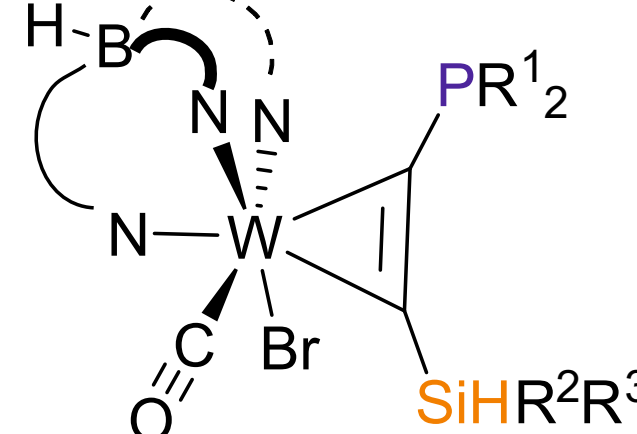
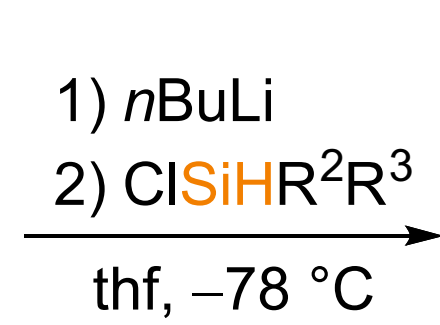
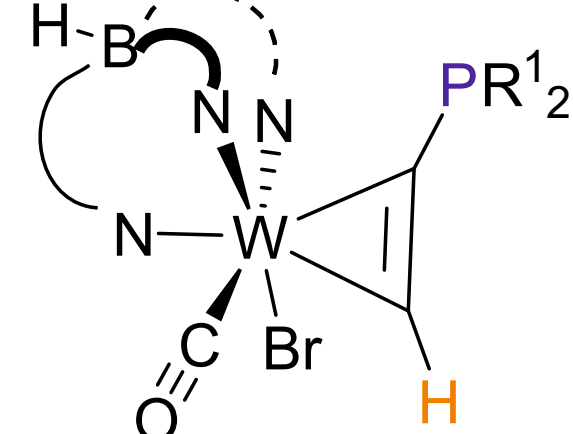
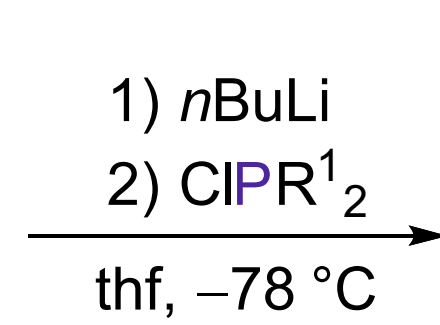
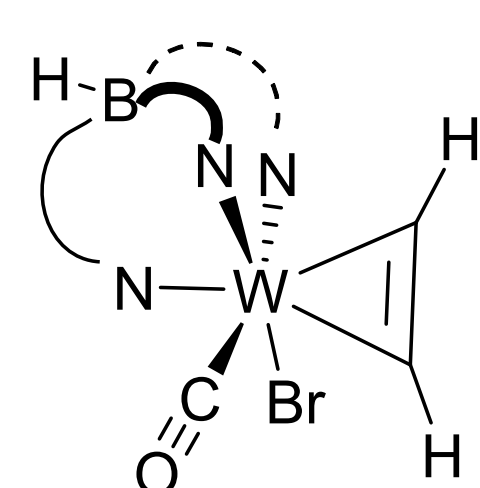


E = -CR<sub>2</sub>, -NR<sub>2</sub>, -NR, -OR,  
-OR', -PR<sub>2</sub>, -SR, -S',  
X = CO, Cl, Br, I, CN<sup>-</sup>, OTf

NEW: Silicon functioning as donor centre

Fig. 1 Overview of possible second and third period donors on the alkyne of a tungsten precursor with variable ligand sphere and donor combinations that have been successfully isolated in polynuclear complexes (table).

SYNTHESIS



R<sup>1</sup> = Ph, *i*Pr  
R<sup>2</sup> = Ph  
R<sup>3</sup> = Ph, H

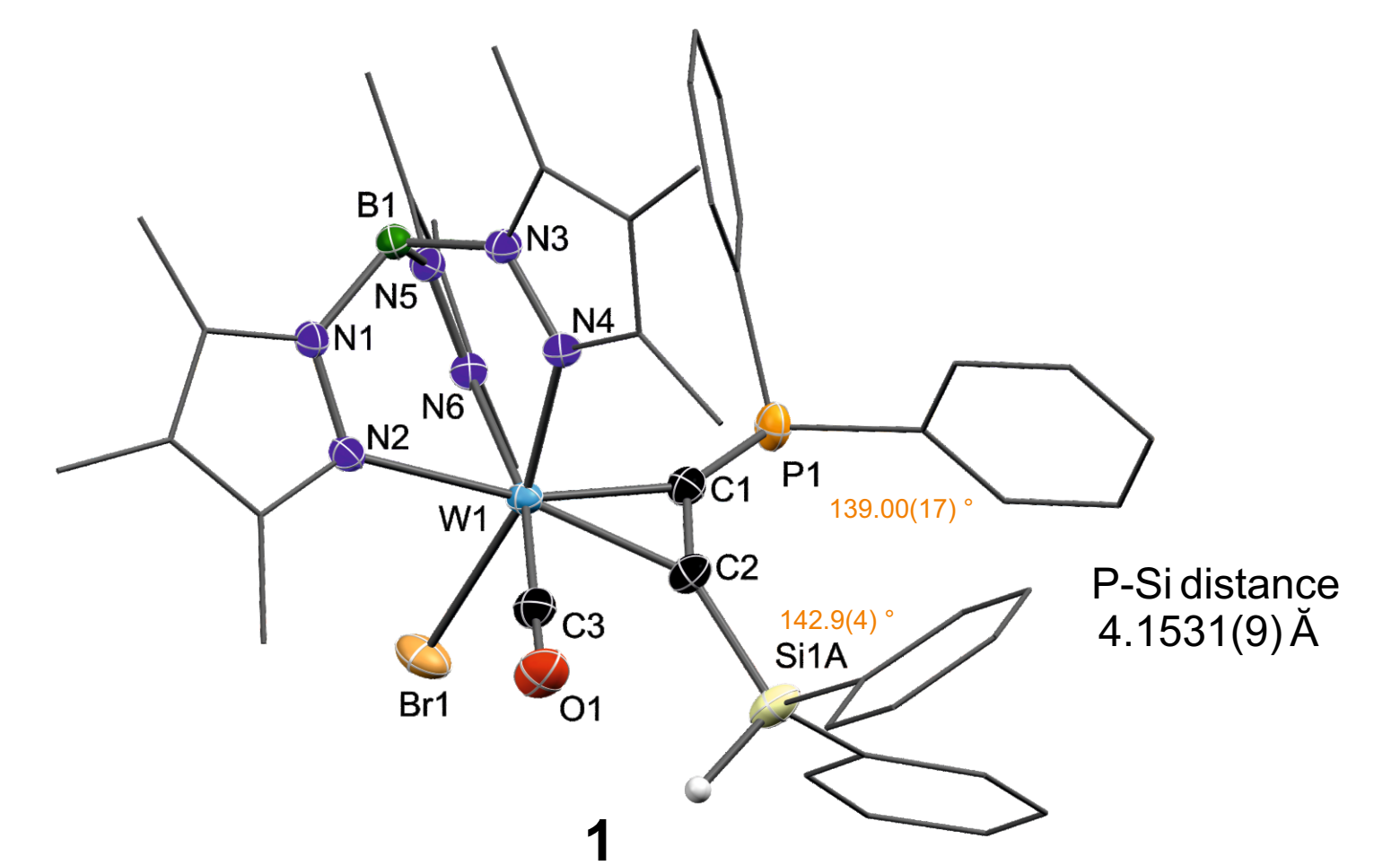
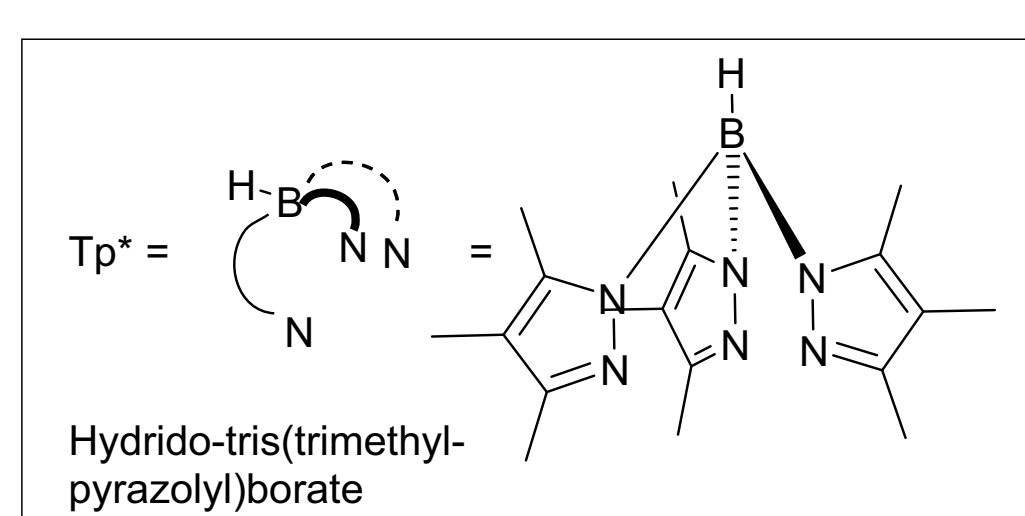


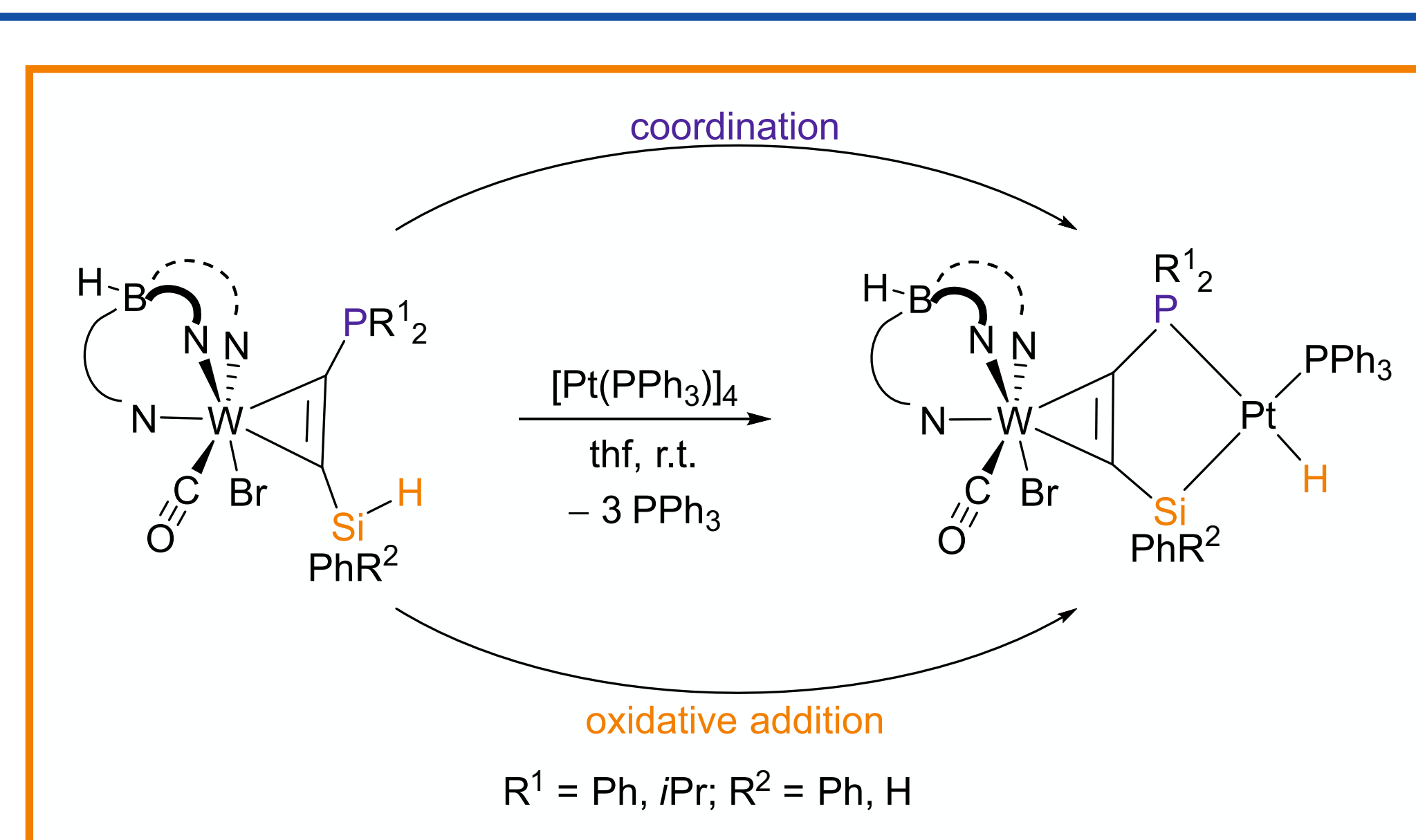
Fig. 2 Molecular structure of P,Si-alkyne complex  $\{[Tp^*W(CO)Br(Ph_2PCCSiHPh_2)]\}$  (1) in the crystal with bend back angles at the alkyne (orange).

ADVANTAGES

- High variability of donors and their substituents
- Redoxactivity
- Highly flexible system enables adjustment of bite angle



Ligand



R<sup>1</sup> = Ph, *i*Pr; R<sup>2</sup> = Ph, H

## Bimetallic Complexes

SYNTHESIS

The  $\alpha$ -P,Si-alkyne ligands can be reacted with precursors of low-valent metals like Pt(0), Ir(I) and Rh(I), that are able to free at least three coordination sites, giving the corresponding hydride chelate complexes **2-4** by coordination of the phosphine and oxidative addition of the Si-H bond.

STRUCTURE

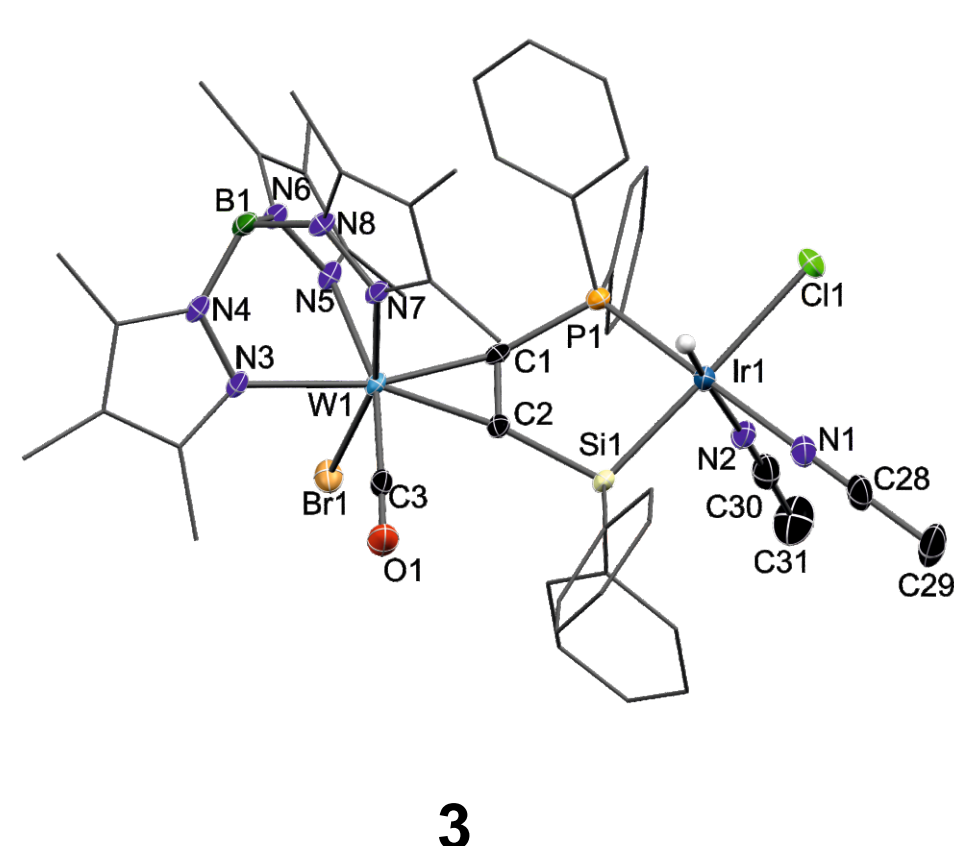


Fig. 3 Molecular structure of  $\{[Tp^*W(CO)Br(Ph_2PCCSiPh_2)]IrH(CH_3CN)_2Cl\}$  (3) in the crystal obtained by reaction of 1 with  $[Ir(COD)Cl]_2$ .

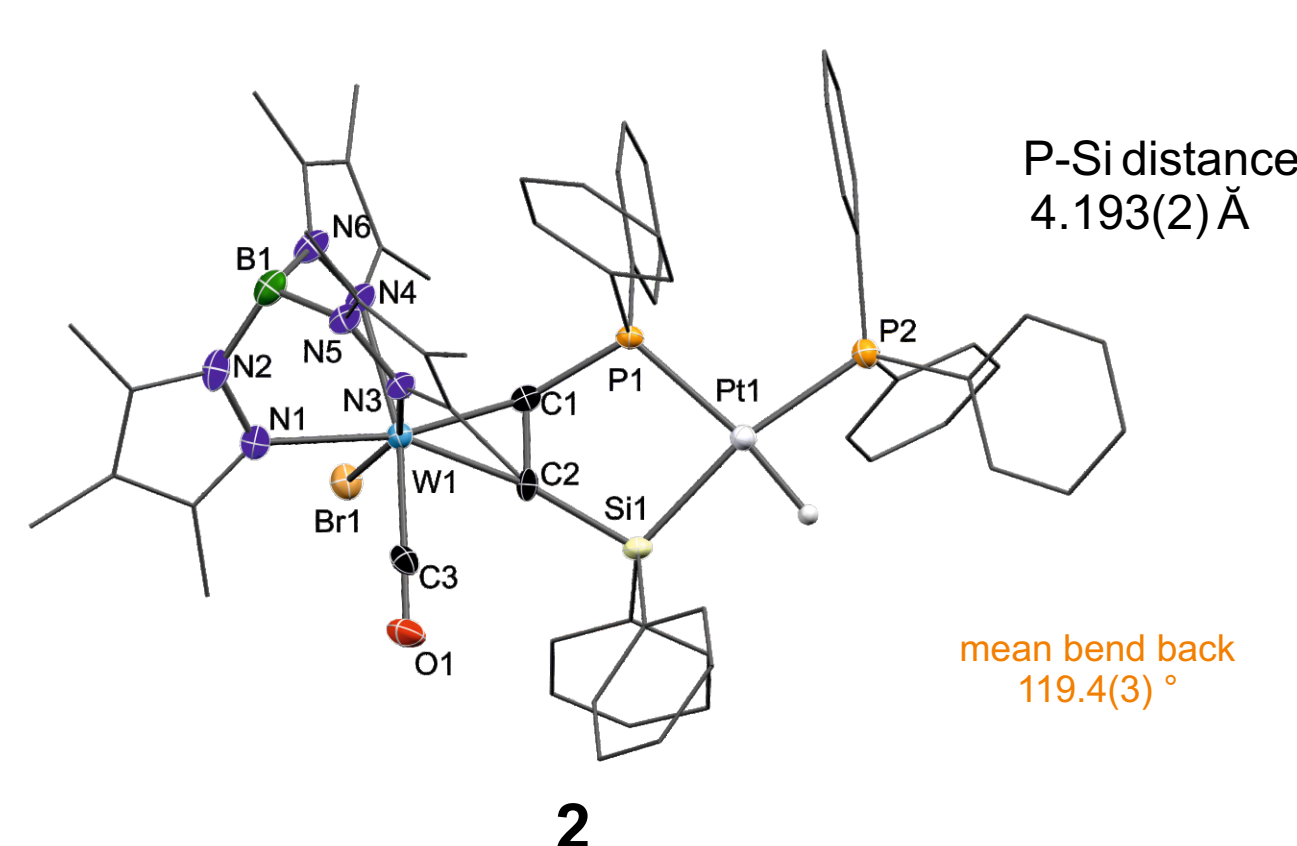


Fig. 4 Molecular structure of  $\{[Tp^*W(CO)Br(Ph_2PCCSiPh_2)]PtH(PPh_3)\}$  (2) in the crystal.

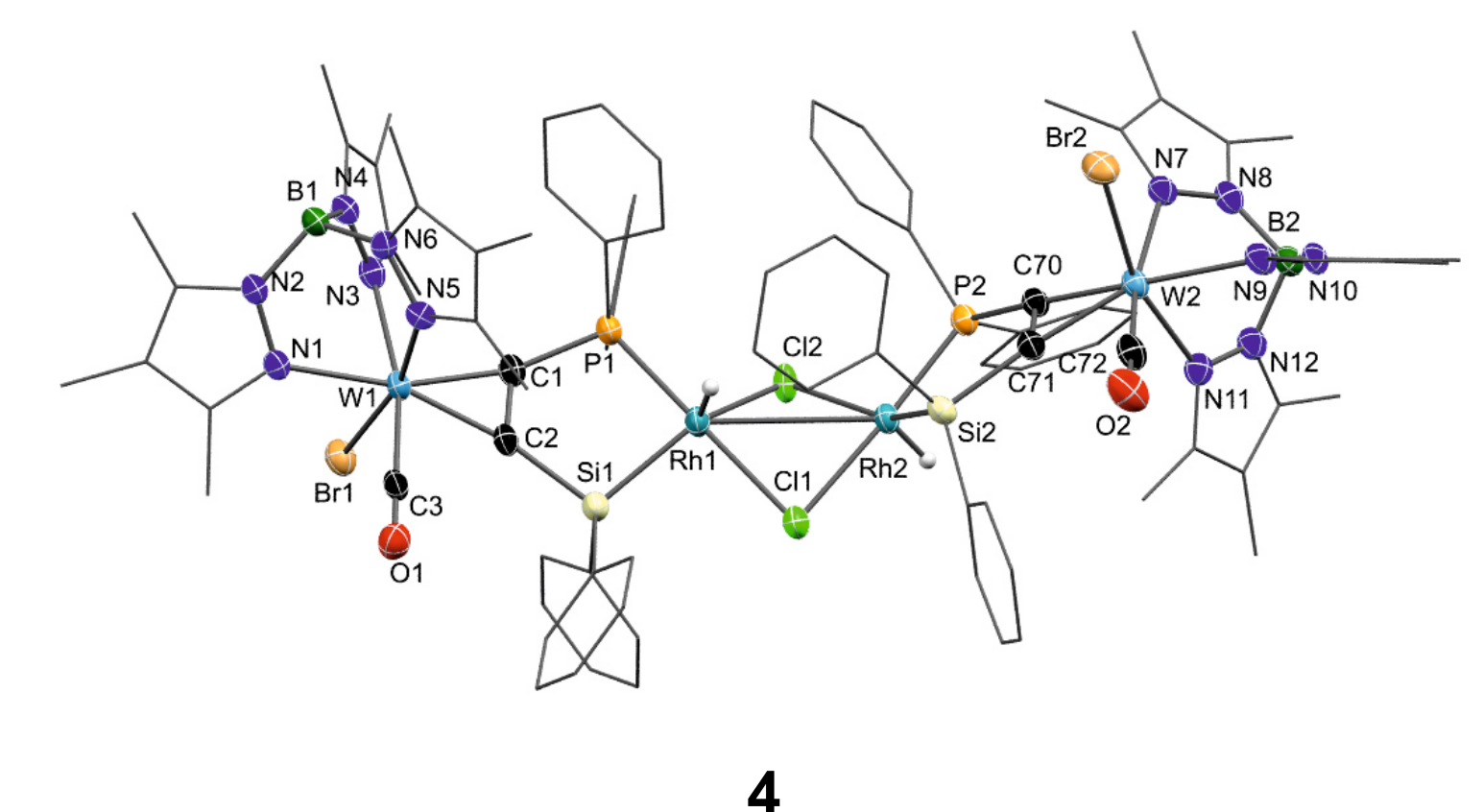


Fig. 5 Molecular structure of  $\{[Tp^*W(CO)Br(Ph_2PCCSiPh_2)]_2Rh_2H_2Cl_2\}$  (4) in the crystal obtained by reaction of 1 with  $[Rh(COD)Cl]_2$ .

MODULATING HYDRIDE REACTIVITY

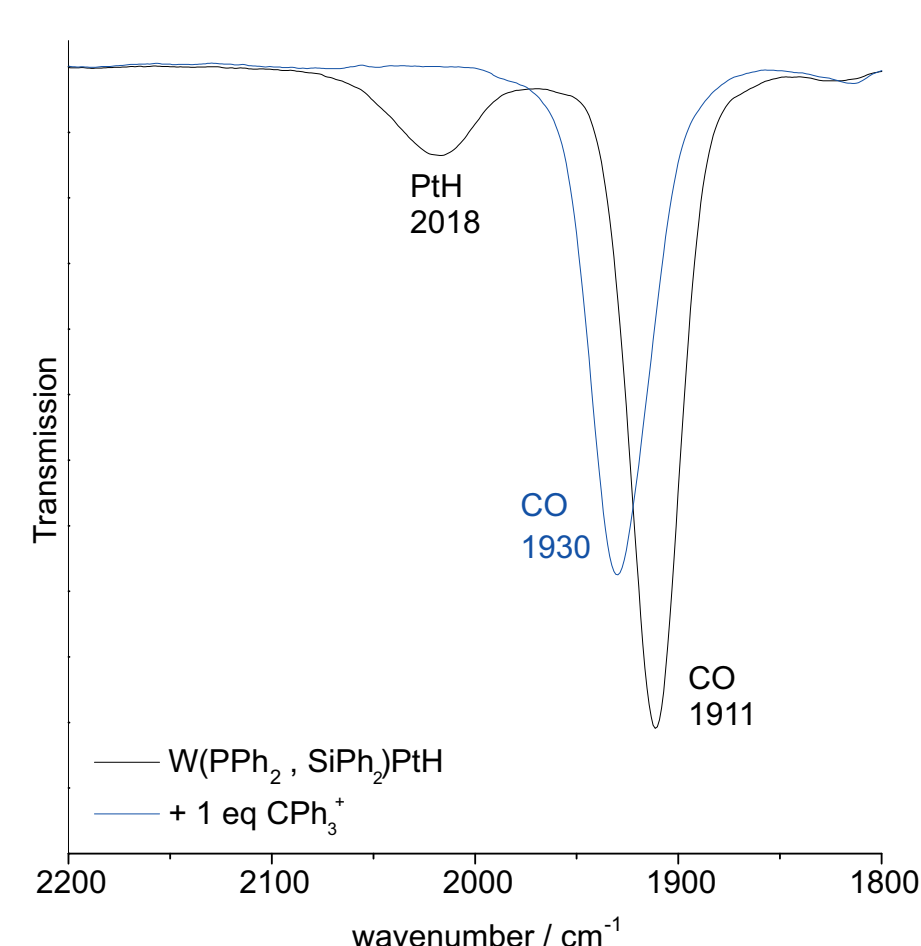


Fig. 6 IR spectra of 1 (black) and the reaction solution after addition of 1 eq.  $CPh_3BF_4$  to 1 (blue) in  $CH_2Cl_2$ .

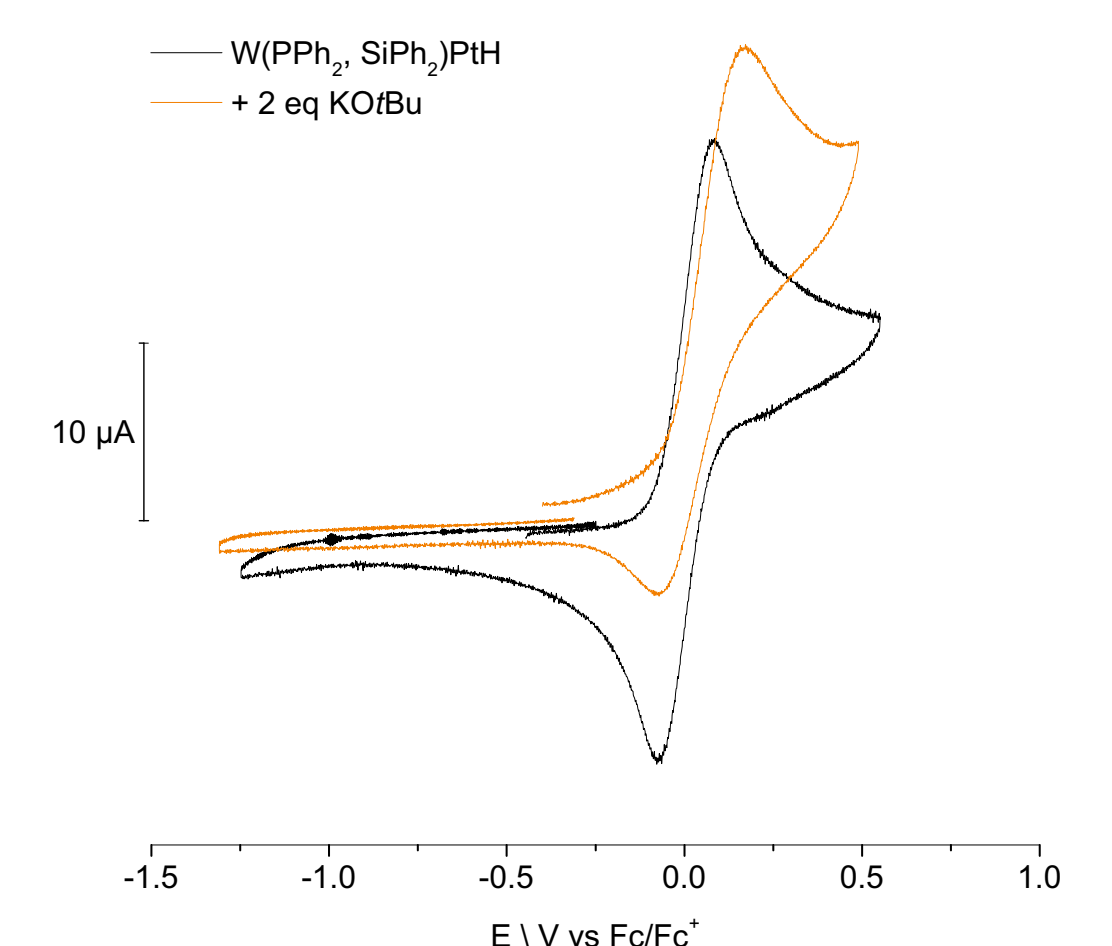
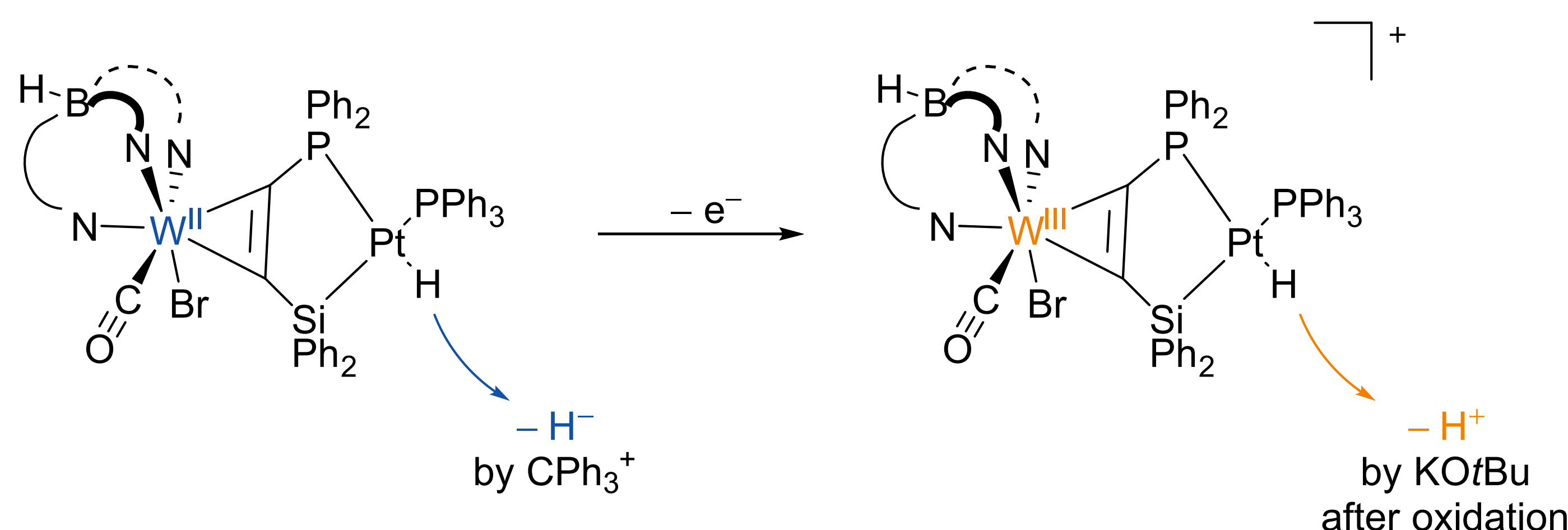


Fig. 7 Cyclic voltammogram of 2 without (black) and with addition of KOtBu (orange) in  $CH_2Cl_2$  (0.1 M Bu<sub>4</sub>NPF<sub>6</sub>, 0.1 V s<sup>-1</sup>).

The platinum bound hydrogen in **2** can be removed by reaction with  $CPh_3BF_4$ , proving the hydridic character. Accordingly, a protic behaviour by reaction with the Brønsted base KOtBu and abstraction of a hydrogen radical with TEMPO could not be observed. The cationic complex resulting from the hydride abstraction could not be isolated so far, but the reaction can be observed by IR and NMR spectroscopy.

Surprisingly, this reactivity can be modulated by the oxidation state of the tungsten as determined by cyclic voltammetry measurements. After addition of KOtBu, the oxidation of **2** is no longer reversible. This finding suggests that deprotonation at the Pt(II) centre is possible after oxidation of the complex. Subsequently, the oxidated species is no longer available for the reductive process.

⇒ UMPOLUNG of Pt-H by OXIDATION ⇐