Universität Rostock

Traditio et Innovatio

Tungsten-Alkyne-Complexes towards Frustrated Lewis Pairs

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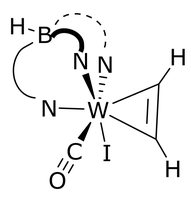
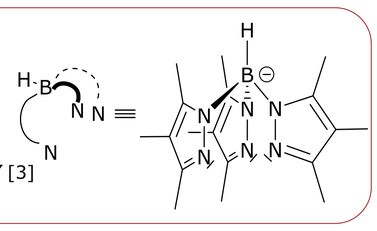
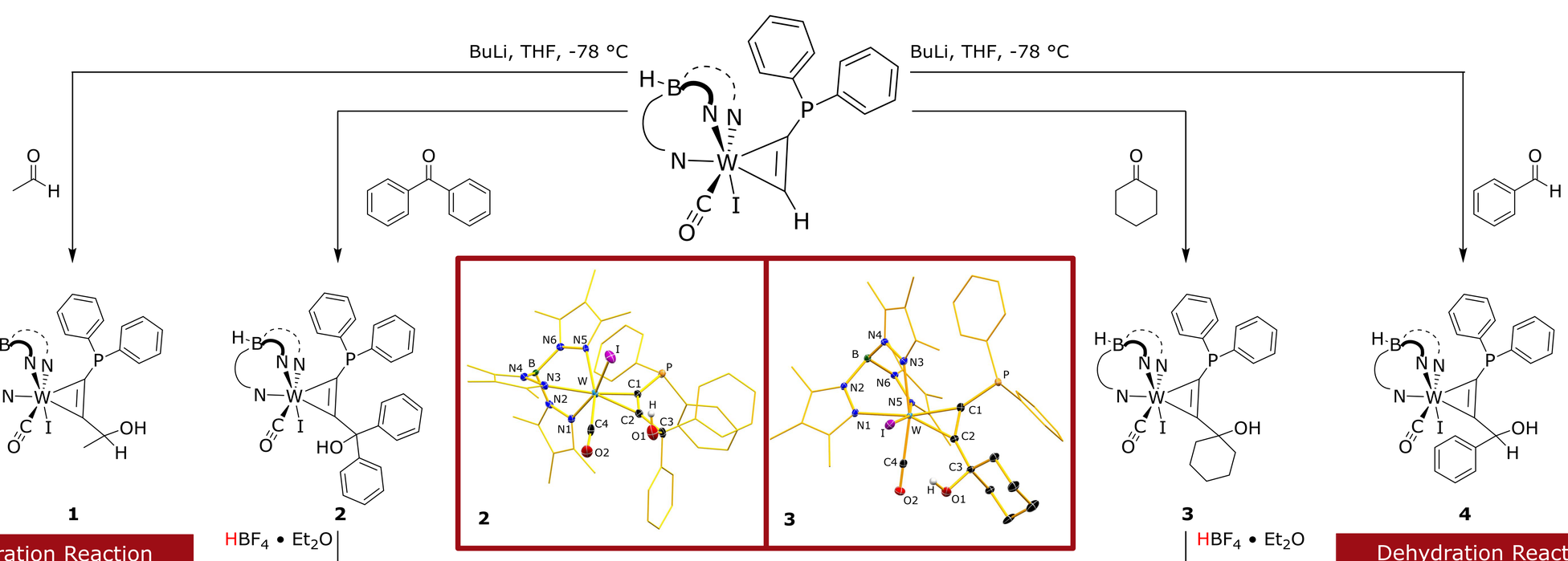
Introduction

We recently developed an efficient template based procedure inspired by TEMPELTON *et al.* for the synthesis of α–donor substituted alkyne ligands. This allows us to modify both α-positions of the coordinated acetylene ligand consecutively.[1,2]



- Anionic
- Tripodal chelating
- Protected from S_E unlike Tp´[3]





Dehydration Reaction Complex **2**

- Protonation of propargyl-complex **2** is probably not centered at the P-atom
- Fast reaction, no P-H bond observable in ^{31}P-NMR-spectra
- Infrared spectra shows CO shift to higher wavenumbers (1933 cm^{-1} to 1986 cm^{-1})

Dehydration Reaction Complex **3**

- Protonation of propagyl-complex **3** occurs at the P-atom
- ^{31}P-NMR-spectra shows doublet due to PH-coupling δ = –2.2 ppm (d)
- Infrared spectra shows CO shift to higher wavenumbers

Intramolecular 1,3-hydrid shift

- Elimination of H_2O led to a 1,3-hydrid shift
- Subsequent electrophilic attack at P resulting in an intramolecular ring closure to phosphonium-cyclohexa-2,5-diene
- Carbenium salt after elimination of H_2O can not be isolated
- Indirect proof of FLP reactivity[4,5]

Carbocation-Phosphine FLP at α-position of alkyne ligand

- Unlike **7-BF$_4$** ring closure is not possible
- Preliminary XRD-analysis indicates a planar Cα and distorted cyclohexyl ring
- This FLP type complex should activate small molecules like CO_2, C_2H_2 and H_2[4,5]

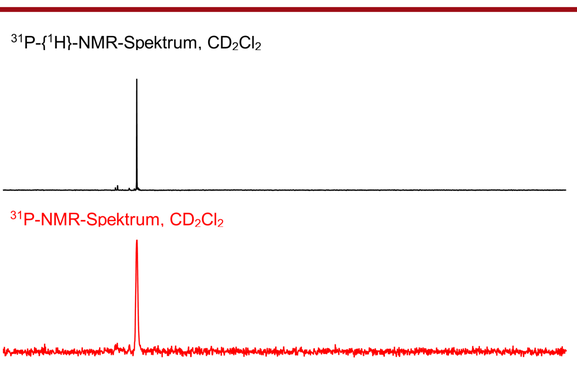


Figure 1 $^{31}P\{^1H\}$ vs. ^{31}P NMR-spectra of **7-BF$_4$**

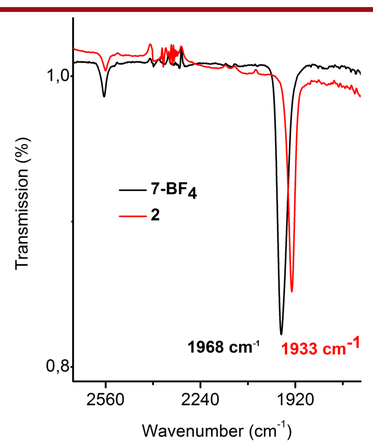


Figure 2 Infrared spectra of **7-BF$_4$** and **2**

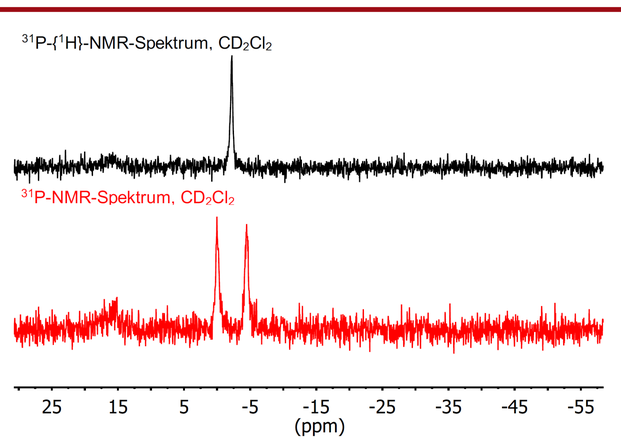


Figure 3 $^{31}P\{^1H\}$ vs. ^{31}P NMR-spectra of **6-BF$_4$**

[1] M. B. Wells, P. S. White, J. L. Templeton, *Organometallics* **1997**, *16*, 1857–1864.
[2] K. Helmdach, A. Villinger, W. W. Seidel, *submitted* **2017**.
[3] Trofimenko, *J. Am. Chem. Soc.* **1967**, *84*, 6288-6294.
[4] D. W. Stephan, G. Erker, *Angew. Chem, Int Ed.* **2010**, *49*, 46-76.
[5] D. W. Stephan, G. Erker, *Angew. Chem, Int Ed.* **2015**, *54*, 4600-4641.

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