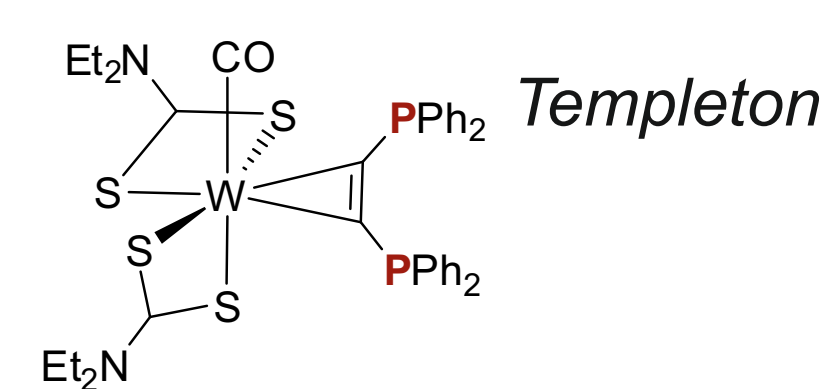
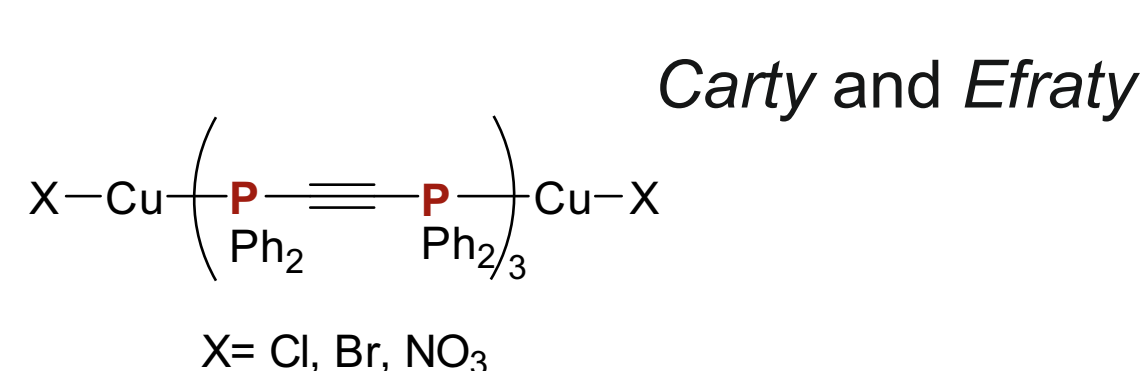
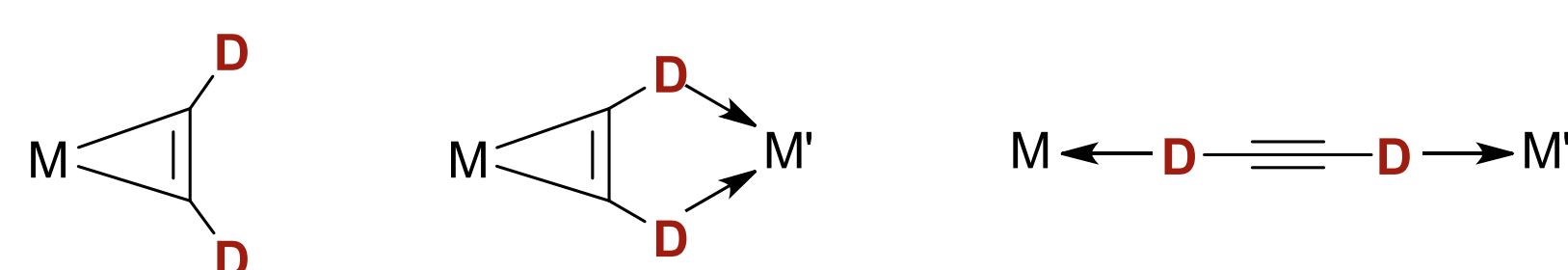


# $\alpha$ -P-Alkyne Complex Ligands

## Synthesis, Basicity and Coordination Chemistry

Paula Thiem, Stephan Ludwig, Alexander Villinger and Wolfram W. Seidel\*

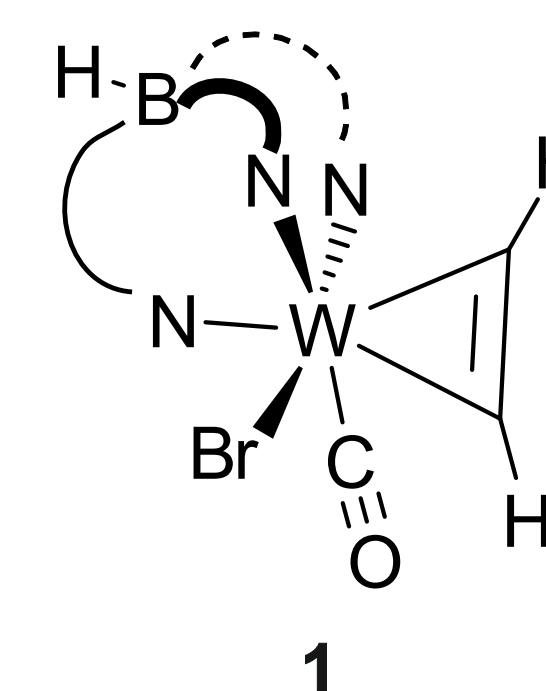
### Introduction



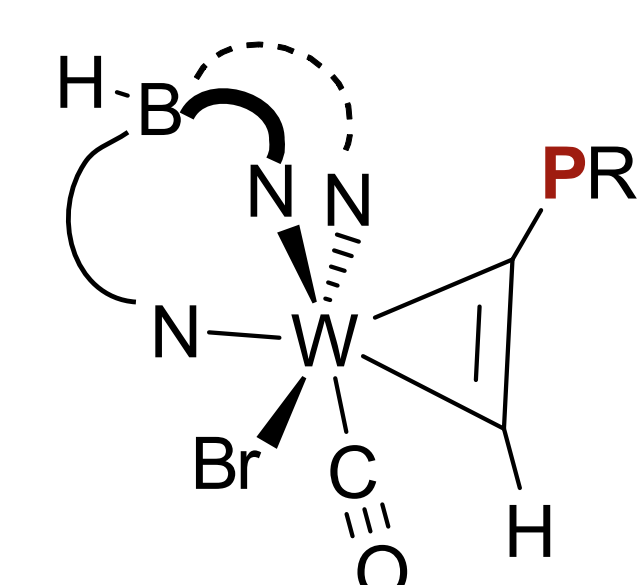
Alkynes substituted by donor atoms in both  $\alpha$ -positions offer the opportunity to combine a redox-active complex moiety with a potentially chelating unit. This makes them valuable building blocks for polynuclear compounds with short metal-metal distances and interesting redox behavior. Coordination of those donor alkynes is possible via the donors or

via the triple bond, but the coordination behavior of P-substituted acetylenes is strongly dominated by the phosphorus. Therefore coordination of diphosphinoalkynes to a metal-precursor mostly leads to  $\kappa^1$ -P-coordination as seen in the example by *Carty and Efraty*.<sup>[1]</sup> The  $\eta^2$ -mode as in the compound published by *Templeton* is obtained less often.<sup>[2]</sup>

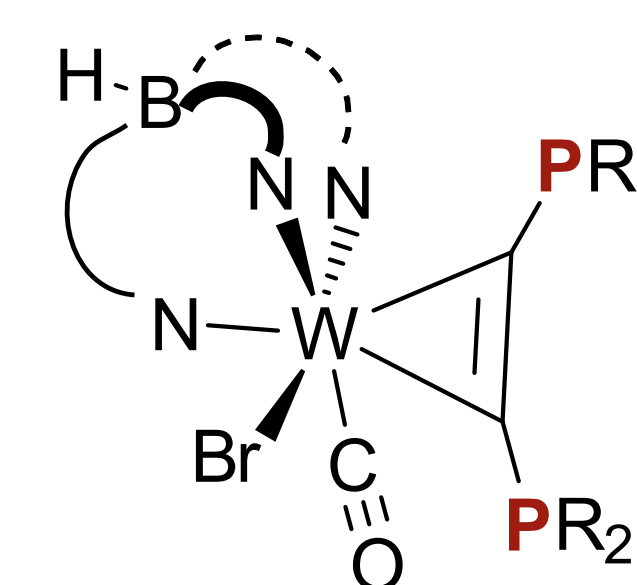
### Synthetic Approach



1) *n*BuLi, -80 °C  
2) ClPR<sub>2</sub>, rt

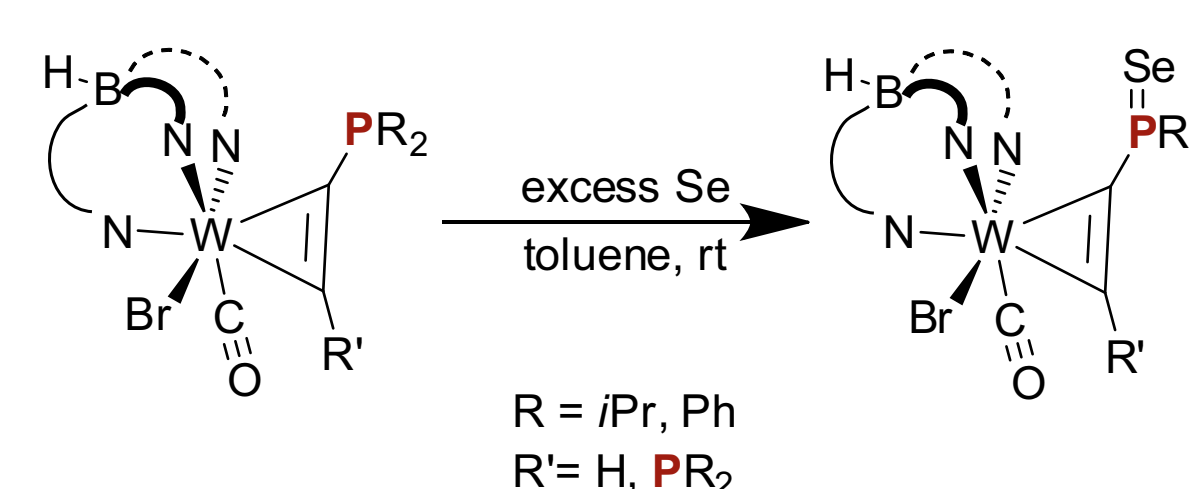


1) *n*BuLi, -80 °C  
2) ClPR<sub>2</sub>, rt



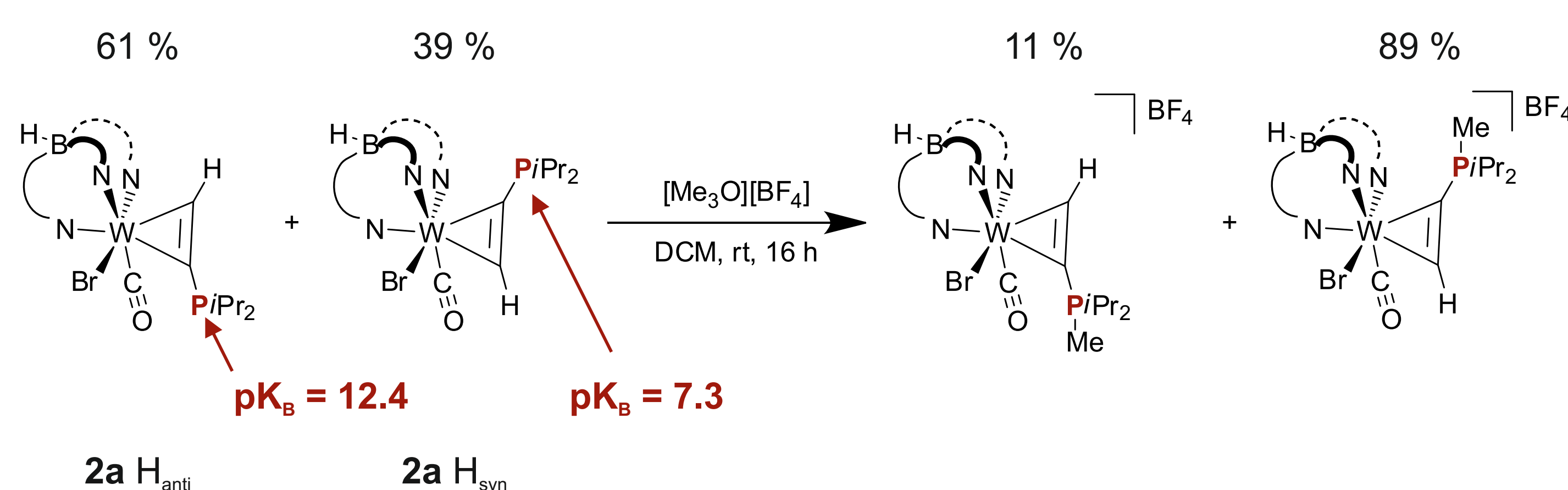
### Basicity of the Phosphine

The  $pK_B$  value of phosphines shows a linear correlation with the <sup>31</sup>P-<sup>77</sup>Se-coupling constant of corresponding P-selenides, which is therefore used as an indirect measure.<sup>[3]</sup> Interestingly, both regioisomers of **2a** differ strongly in their basicity, with **2a** ( $H_{anti}$ ) even lying in the range of **2b**. In the diphosphanes **3** both phosphane positions also show a slight difference in this regard. It is known that the substituents of a phosphine strongly affect its basicity. Here, the replacement of phenyl substituents by isopropyl groups leads to an increase of the phosphine basicity by several orders of magnitude.

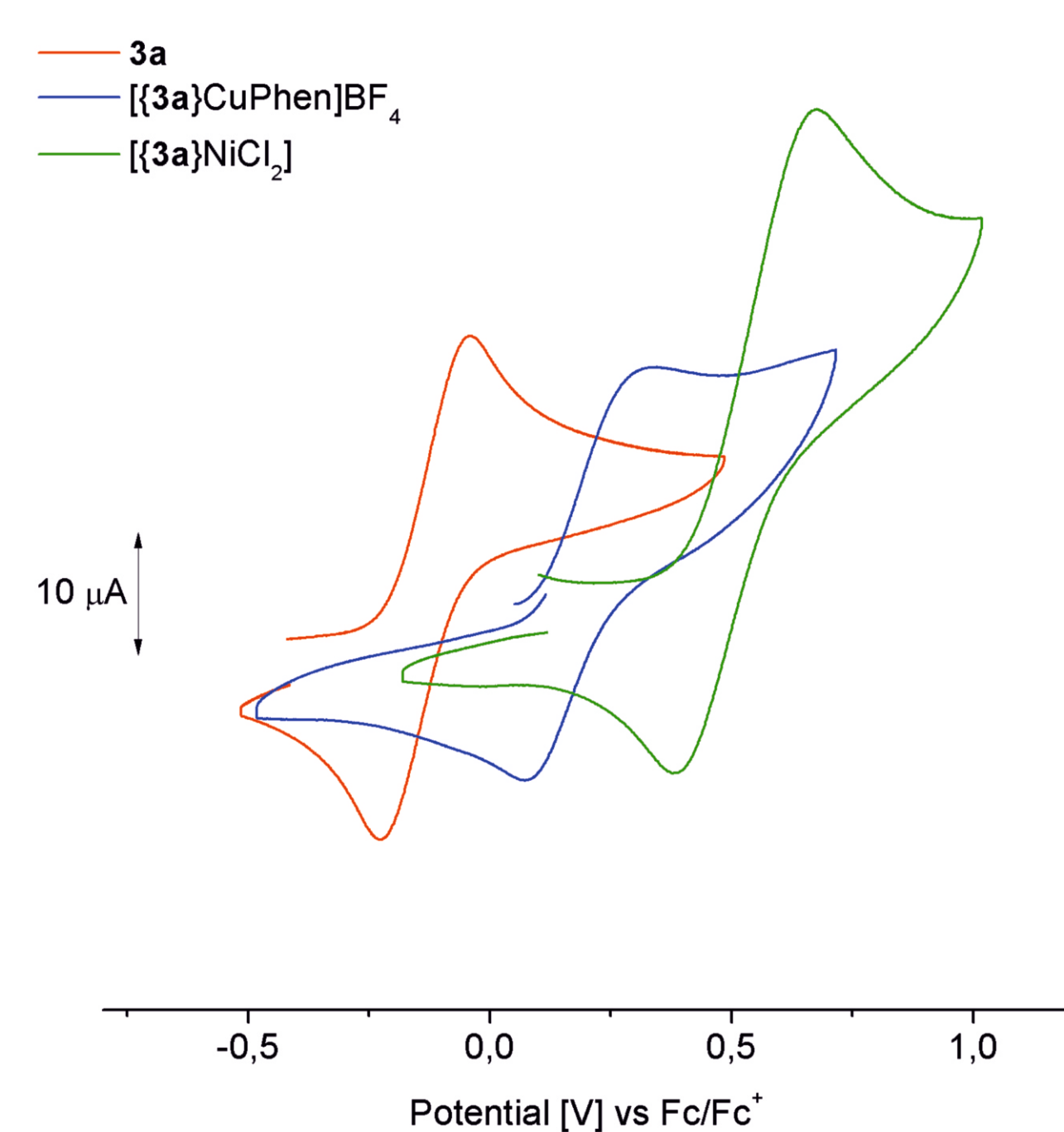
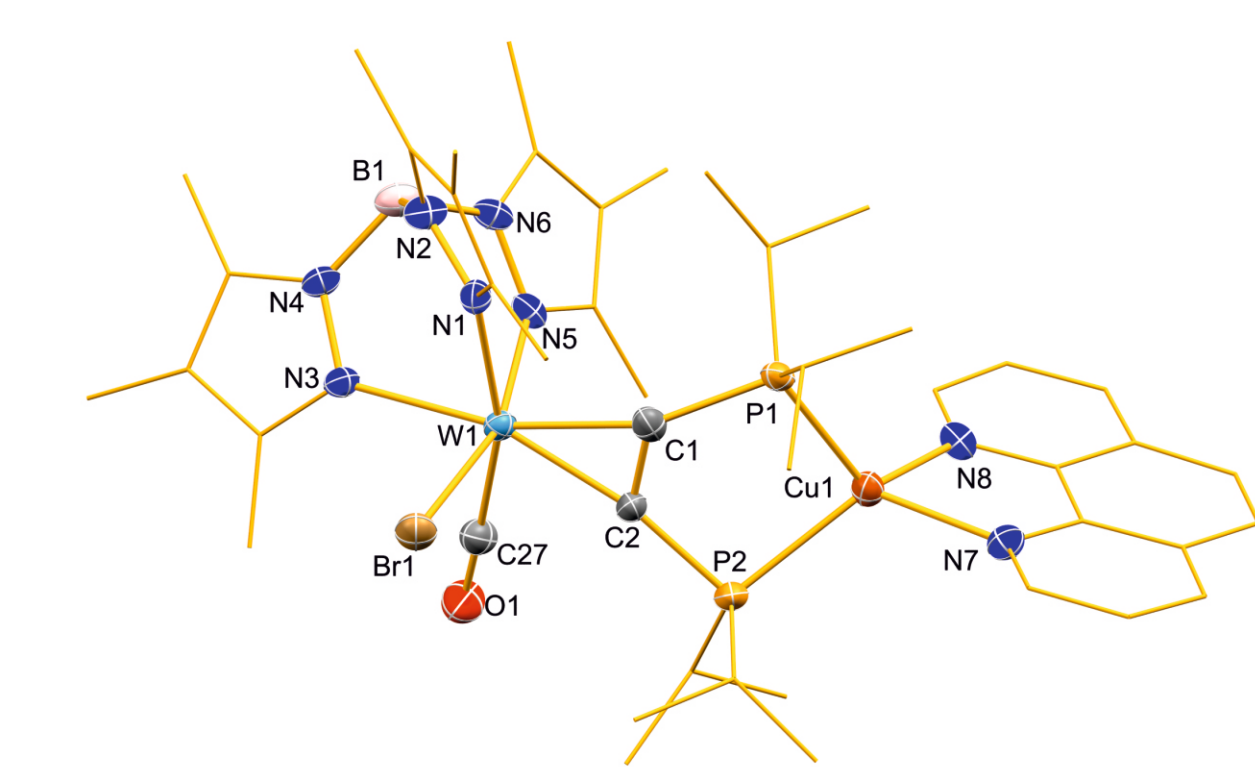


	<sup>1</sup> J <sub>PSe</sub>	est. pK <sub>B</sub>
Monophos <b>2a</b> H <sub>syn</sub>	701.2	7.3
<b>2a</b> H <sub>anti</sub>	740.2	12.4
<b>2b</b>	738.5	12.2
Diphos <b>3a</b>	697.1	6.7
	691.9	6.0
<b>3b</b>	769.9	16.3
	764.7	14.3

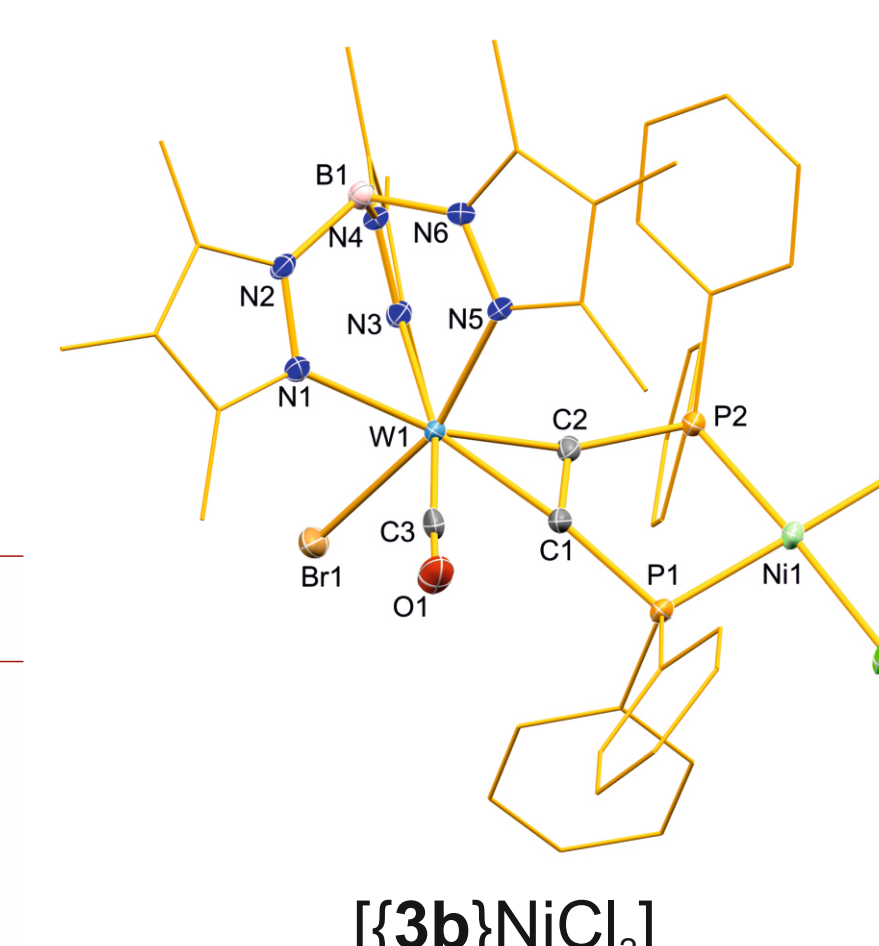
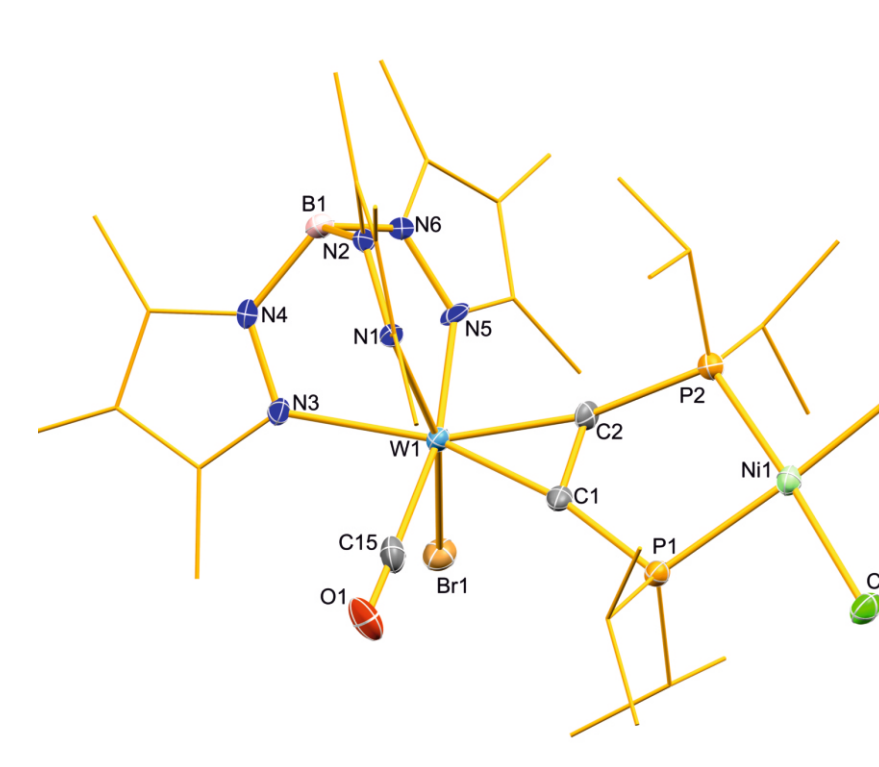
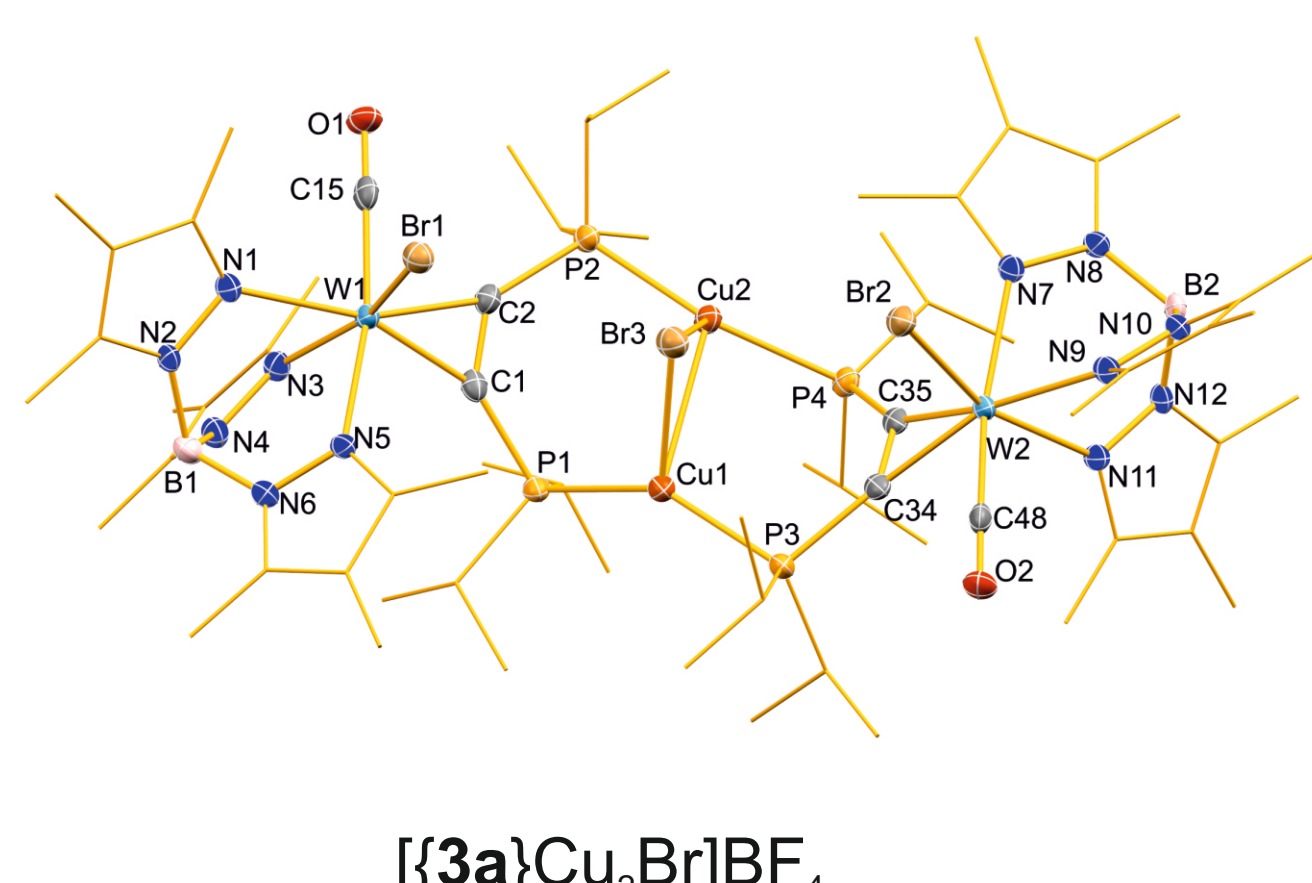
The significant difference in basicity between the isomers of **2a** is confirmed by methylation of the phosphorus. The inversion of the isomer ratio is based on the more rapid methylation of the H<sub>syn</sub> isomer and rotation of the alkyne.



### Use as Chelating Ligand

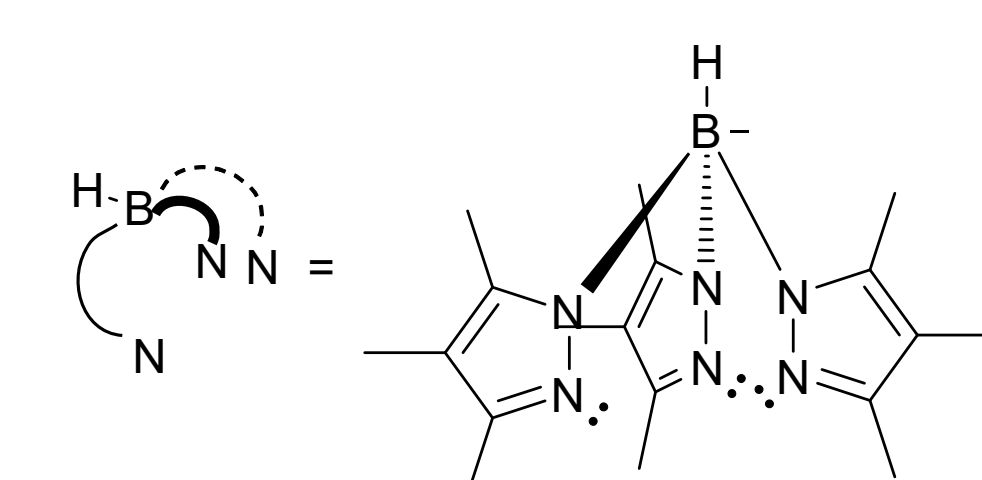


	[[ <b>3a</b> ] <sub>2</sub> CuPhen]BF <sub>4</sub>	[[ <b>3a</b> ] <sub>2</sub> Cu <sub>2</sub> Br]BF <sub>4</sub>	<b>3a</b>
Cu1-P1 [Å]	2.694(13)	2.282(2)	-
C2-C1-P1	121.5(4)	135.8(4)	153.9(2)
P1-P2 [Å]	3.271	3.834	4.41



In previous works we prepared polynuclear compounds by coordination of diphosphanes **3** to transition metals as Pt(II)<sup>[4]</sup> while binding to first row transition metals could not be achieved so far due to a lack of basicity of commonly used **3b**. However, the newly investigated, more basic diphosphine **3a** is able to coordinate Cu(I) and Ni(II) giving complexes stable in solution. The Ni(II) complex can also be obtained with **3b**, though the lower donor strength is reflected in the strongly reduced stability.

Electrophilic substitution after coordination of the unsubstituted acetylene allows functionalization whereas the side-on binding mode is maintained. While investigation of P-substituted acetylene compounds is usually restricted to those of bis(diphenylphosphino)acetylene (dppa), this synthesis enables variation of the substituents on the phosphorus. Due to stabilizing  $\pi$ -interactions between one phenyl group and the scorpionate ligand, the first substitution step is regioselective with diphenylphosphine while synthesis of **2a** gives two regioisomers in a ratio of 39 % (H<sub>syn</sub>) to 61 % (H<sub>anti</sub>).



Hydrido-tris(trimethylpyrazolyl)borate

[1] A. J. Carty, A. Efraty, *Can. J. Chem.* **1968**, *4*, 1598–1599.

[2] B. C. Ward, J. L. Templeton, *J. Am. Chem. Soc.* **1980**, 1532–1538.

[3] U. Beckmann, D. Süslüyan, P. C. Kunz, *Phosphorus Sulfur Silicon Relat. Elem.* **2011**, *186*, 2061–2070.

[4] K. Helmdach, S. Dörk, A. Villinger, W. W. Seidel, *Dalton Trans.* **2017**, *46*, 11140–11144.