

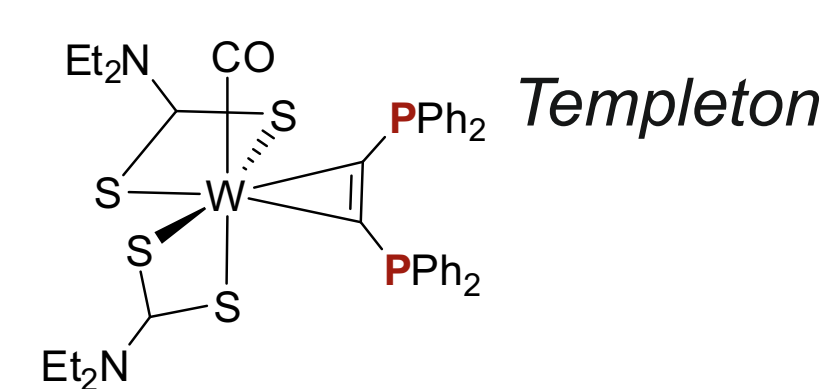
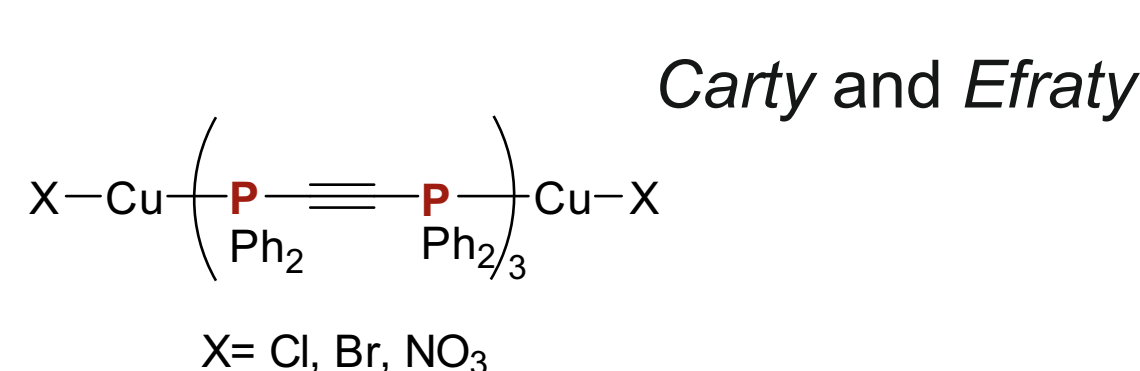
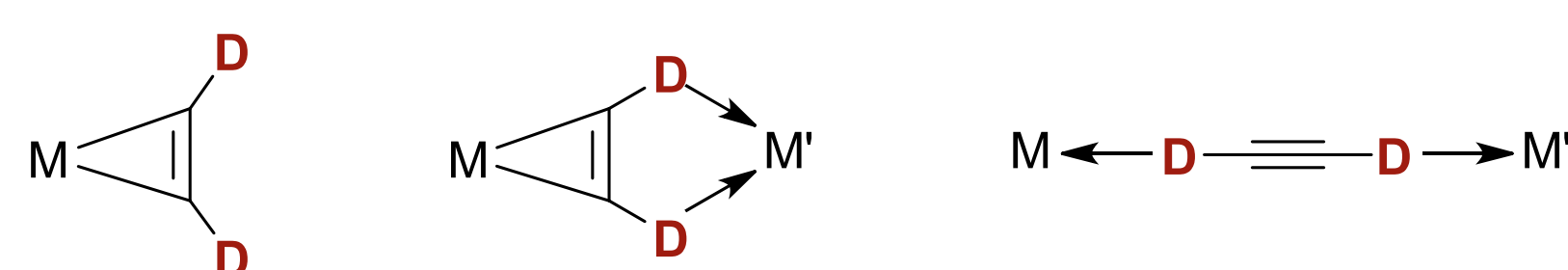


α -P-Alkyne Complex Ligands

Synthesis, Basicity and Coordination Chemistry

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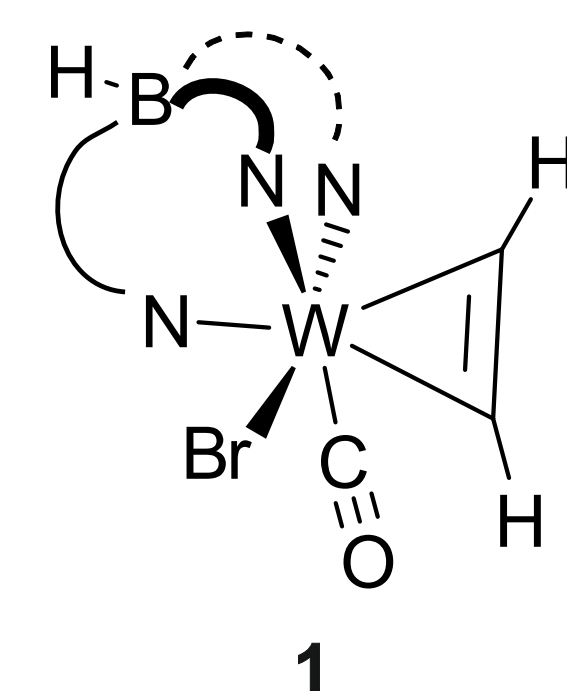
Introduction



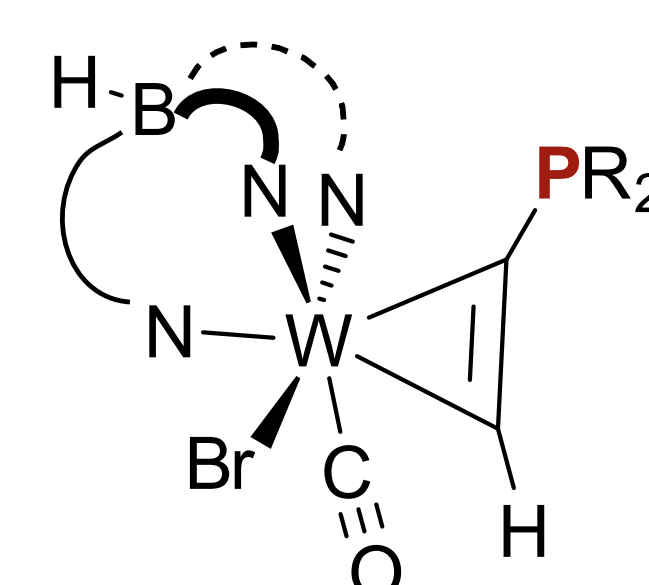
Alkynes substituted by donor atoms in both α -positions offer the opportunity to combine a redox-active complex moiety with a potentially chelating unit. This makes them valuable building blocks for polynuclear compounds with short metal-metal distances and interesting redox behavior. Coordination of 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 κ^1 -P-coordination as seen in the example by Carty and Efraty.^[1] The η^2 -mode as in the compound published by Templeton is obtained less often.^[2]

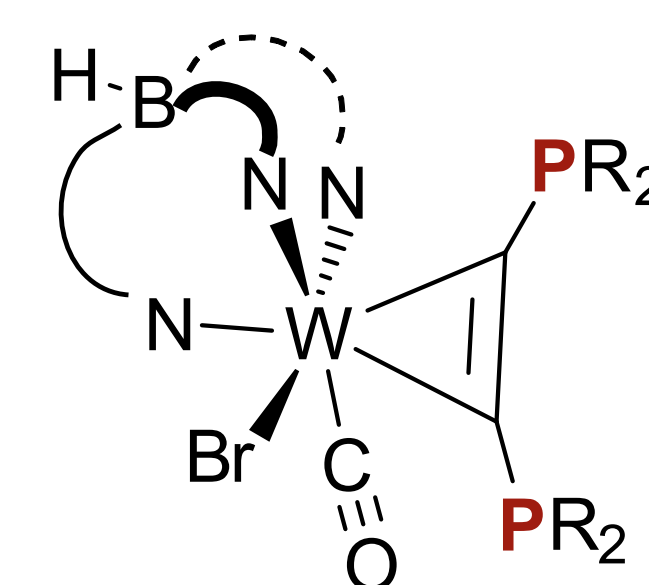
Synthetic Approach



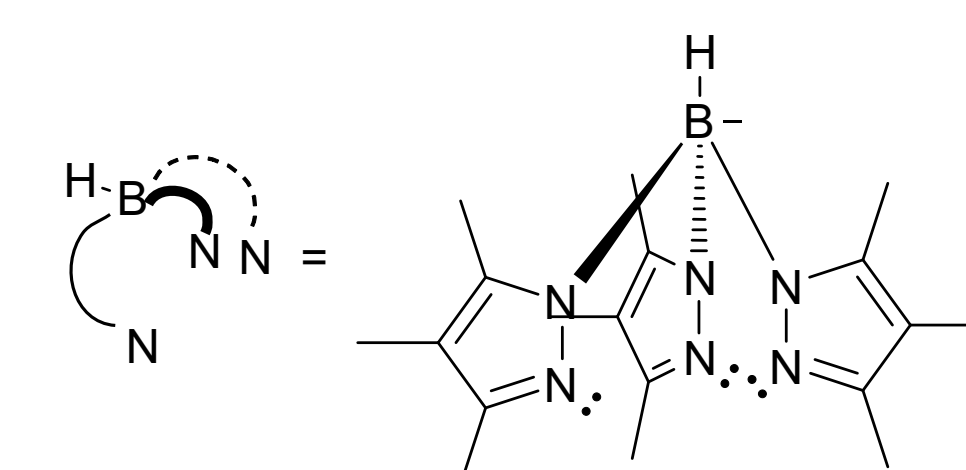
1) *n*BuLi, -80 °C
2) ClPR₂, rt



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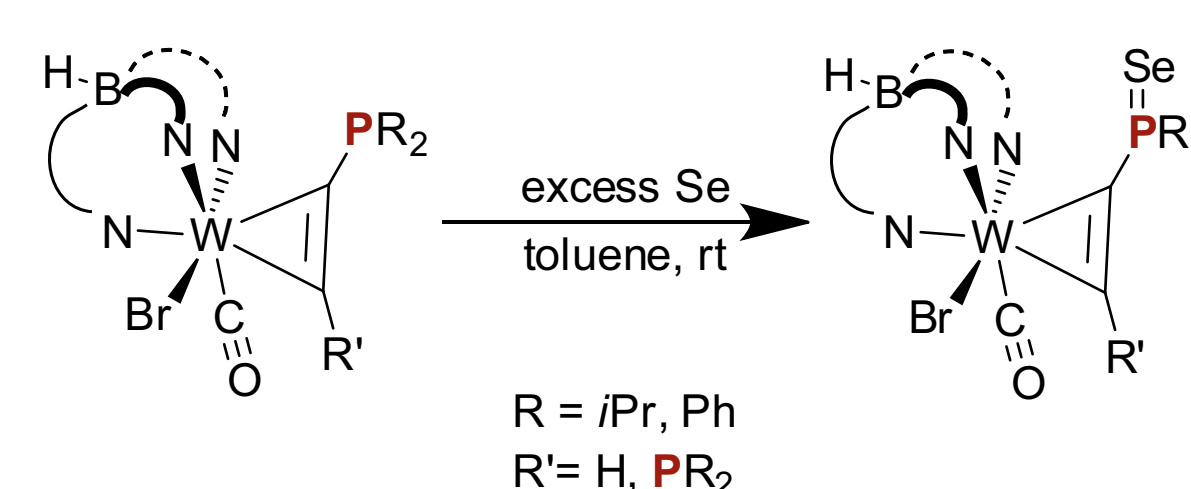
Electrophilic substitution after coordination of the unsubstituted acetylene allows functionalization whereas the side-on binding mode is maintained. While investigation of P-substituted acetylene compounds is usually restricted to those of bis(diphenylphosphino)acetylene (dppa), this synthesis enables variation of the substituents on the phosphorus. Due to stabilizing π -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_{syn}*) to 61 % (*H_{anti}*).



Hydrido-tris(trimethylpyrazolyl)borate

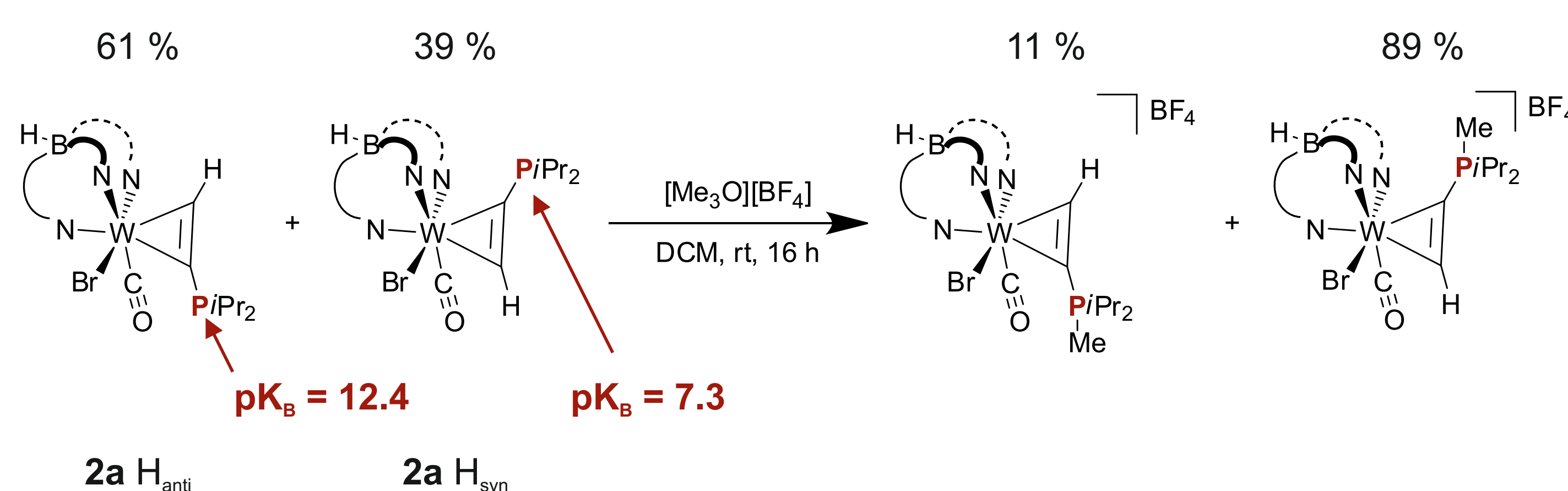
Basicity of the Phosphine

The pK_B value of phosphines shows a linear correlation with the ^{31}P - ^{77}Se -coupling constant of corresponding P-selenides, which is therefore used as an indirect measure.^[3] 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.

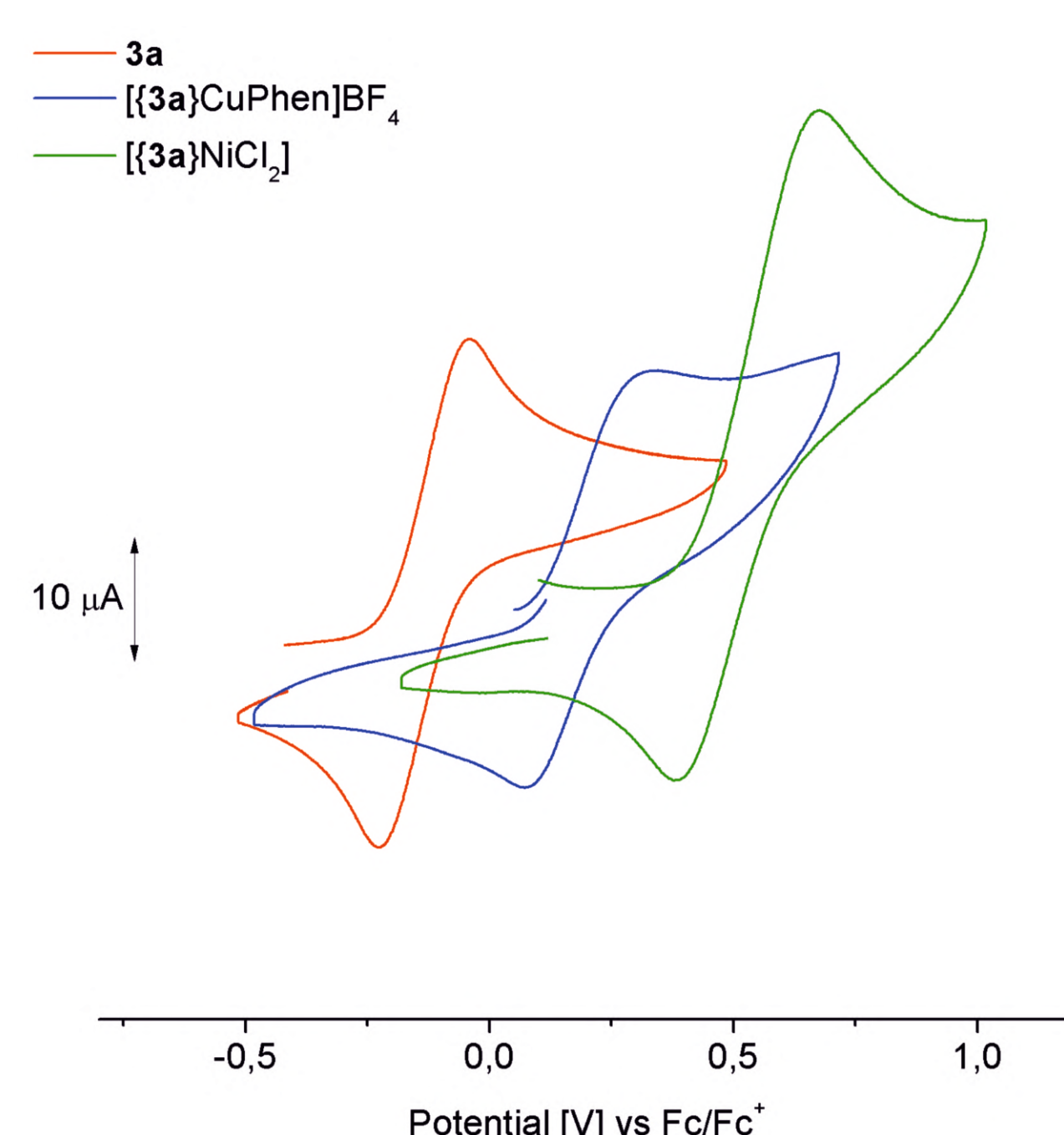
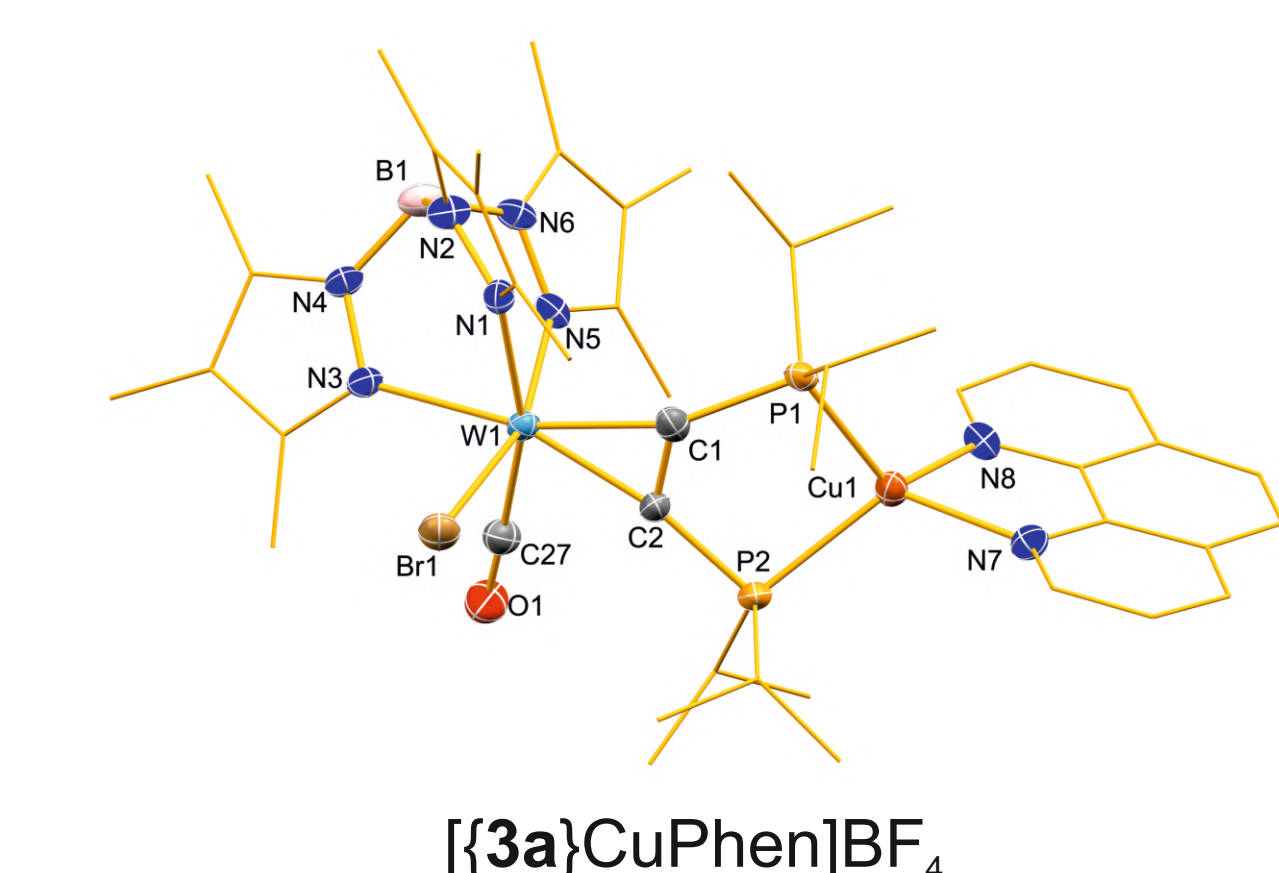


	$^1J_{\text{PSe}}$	est. pK_B
Monophos 2a <i>H_{syn}</i>	701.2	7.3
2a <i>H_{syn}</i>	740.2	12.4
2b	738.5	12.2
Diphos 3a	697.1	6.7
	691.9	6.0
3b	769.9	16.3
	764.7	14.3

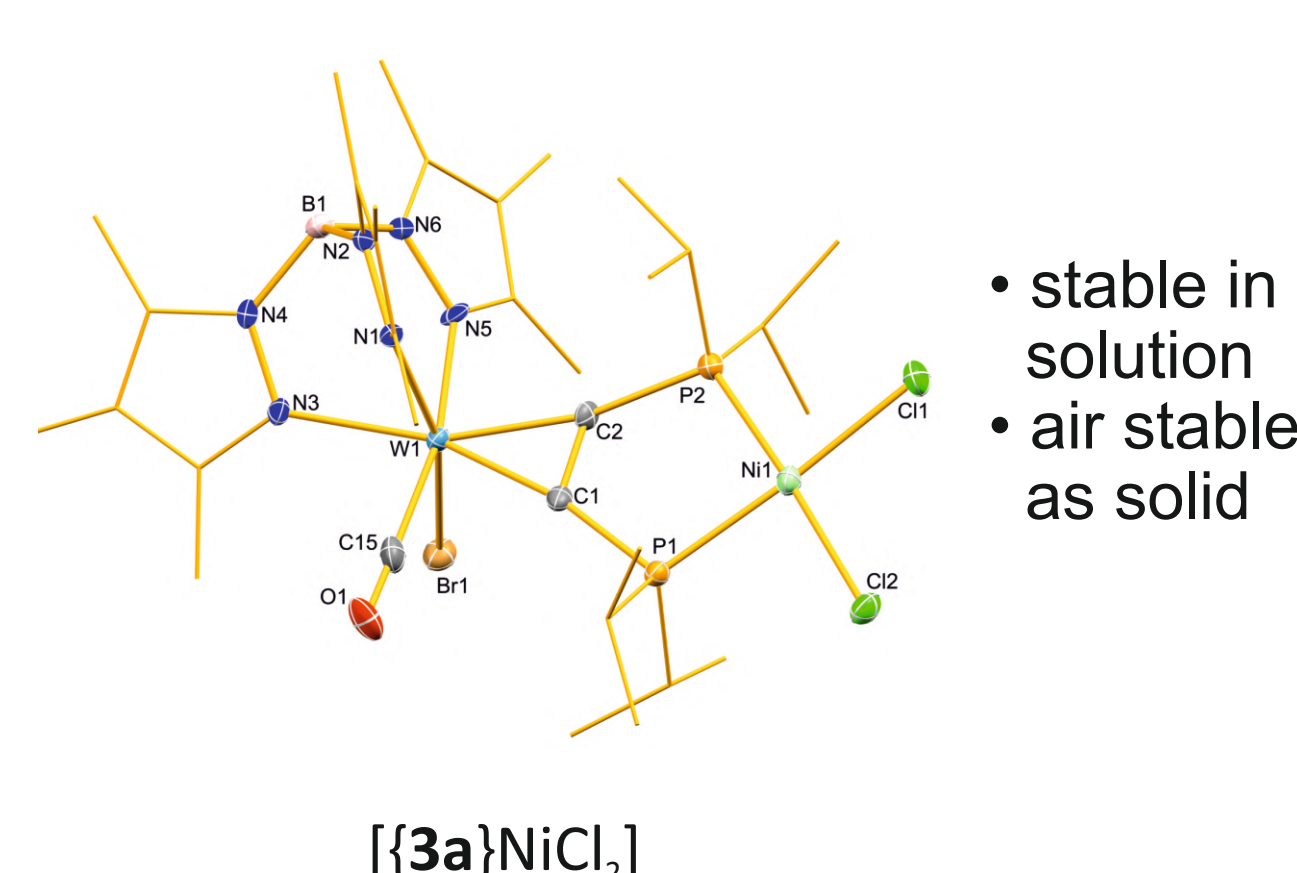
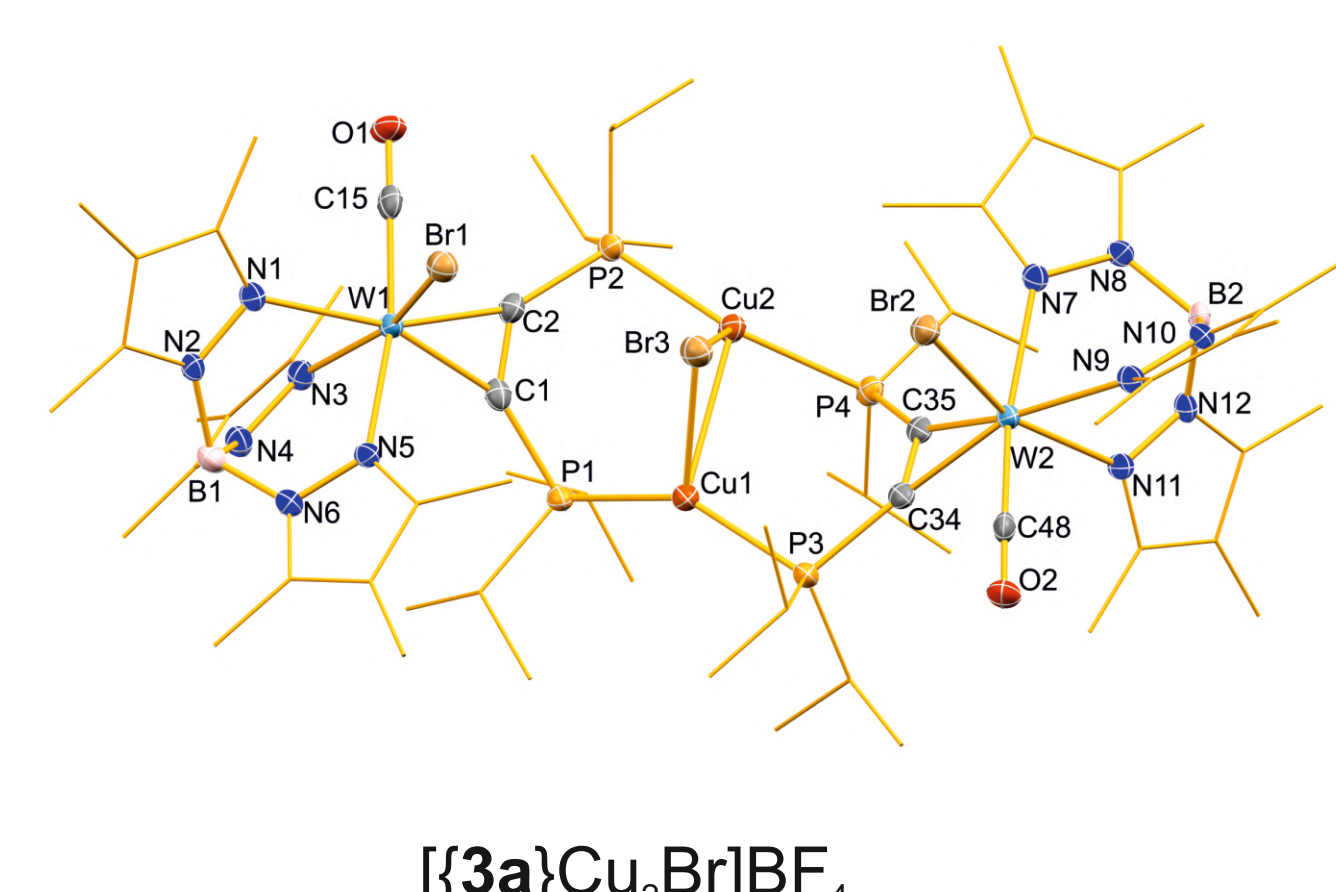
The significant difference in basicity between the isomers of **2a** is confirmed by methylation of the phosphorus. The inversion of the isomer ratio is based on the more rapid methylation of the *H_{syn}* isomer and rotation of the alkyne.



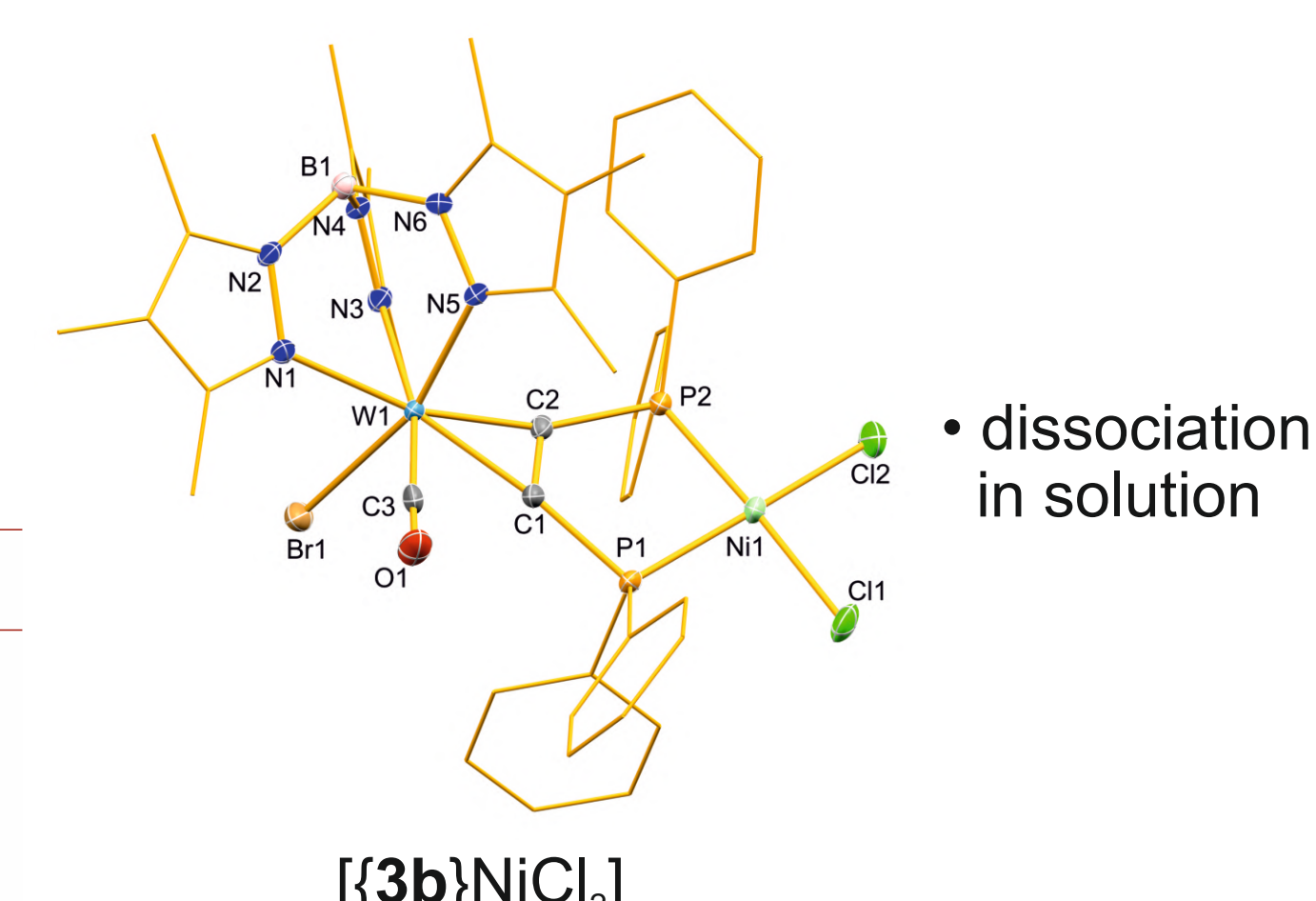
Use as Chelating Ligand



	[{ 3a }CuPhen]BF ₄	[{ 3a }Cu ₂ Br]BF ₄	3a
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



vs.



In previous works we prepared polynuclear compounds by coordination of diphosphanes **3** to transition metals as Pt(II)^[4] 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.

[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.