

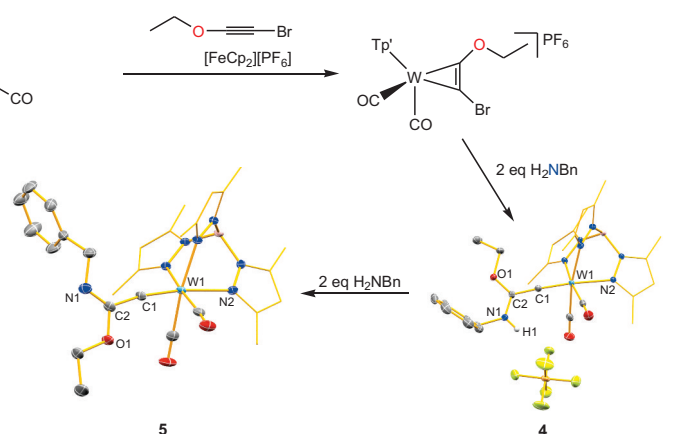
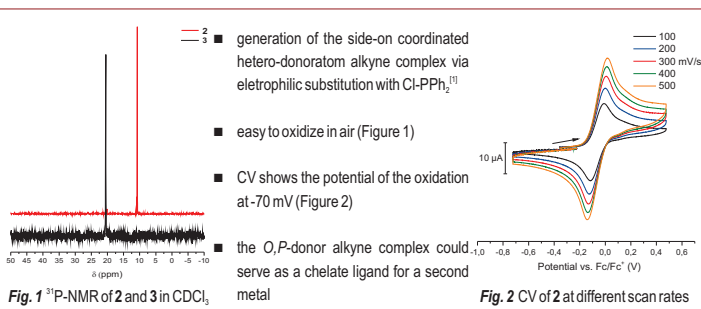
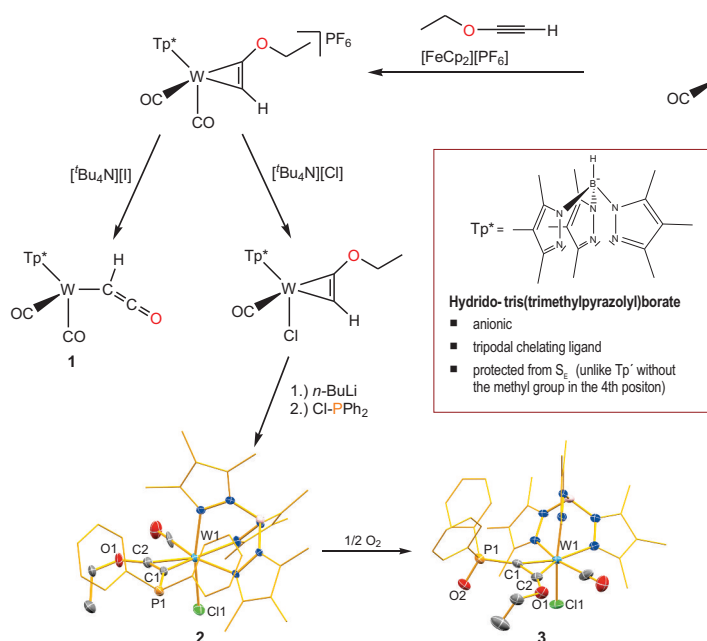


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Electrophilic Substitution

VS

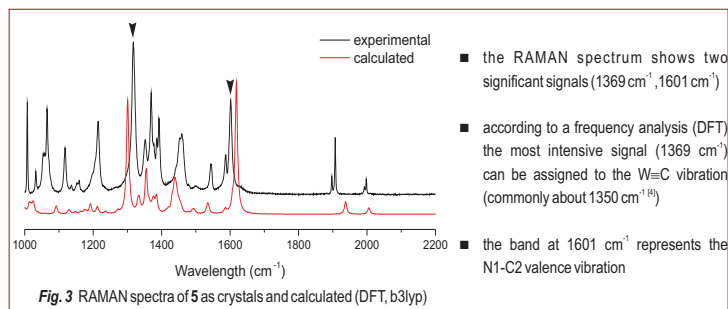
Nucleophilic Substitution



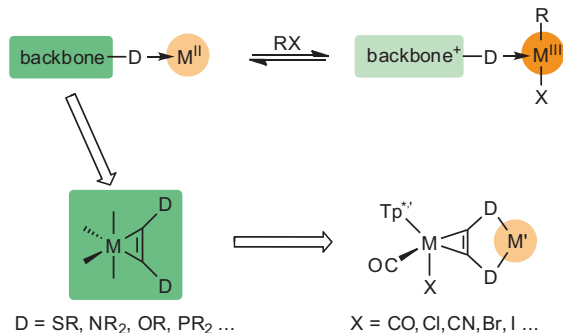
- synthetic goal: generation of side-on coordinated α -donor-alkyne complexes with nucleophiles^[2]
- the nucleophile causes a rearrangement of the alkyne to a carbenium-carbyne^[3]
- the positive charge is delocalized over the π -bonding system of the carbenium-carbyne-ligand
- excess of amine leads to the deprotonation of the nitrogen (N1)

Selected bond lengths [Å]

	4	5
W1-C1	1.828(2)	1.813(4)
W1-N2	2.260(2)	2.296(3)
C1-C2	1.429(3)	1.456(5)
C2-O1	1.311(3)	1.366(4)
C2-N1	1.317(3)	1.271(5)

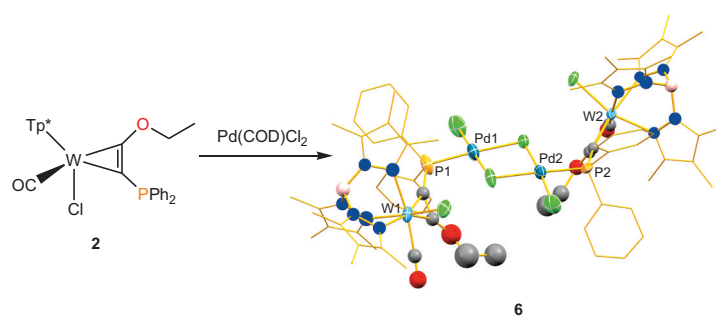


Metalloligands as backbones for catalysis



- research on redoxactive donor-substituted alkyne complexes and their possibility to coordinate on catalytic active metals showing M-L cooperativity^[5]
- metalloligand enables the two electron oxidative addition step on M' (the metal is oxidized only once)
- possible to get catalytic noble metal like reactivity with first row transition metals

Complex 2 as a functional metalloligand



- coordination of the metalloligand 2 at palladium leads to the complex 6
- the dimerisation of the complex is favoured over the coordination of the ether group
- leading to the idea, that the ether group can be used as a pendant arm function (with more oxophilic metals than palladium)^[6]

[1] W.W. Seidel, K. Helmdach, S. Ludwig, A. Villinger, 2017, submitted.

[2] J. Rüger, Ch. Timmermann, A. Villinger, A. Hinz, D. Hollmann, W. W. Seidel, *Chem. Eur. J.* 2016, 22, 11191-11195.

[3] K. Helmdach, J. Rüger, A. Villinger, W. W. Seidel, *Chem. Commun.* 2016, 52, 2616-2619.

[4] Z. Xu, A. Mayr, I. S. Butler, *J. Organomet. Chem.* 2002, 648, 93-98.

[5] V. Lyaskovskyy, B. de Bruin, *ACS Catal.* 2012, 2, 270-279.

[6] A. Bader, E. Lindner, *Coord. Chem. Rev.* 1991, 108, 27-110.