Universität Rostock

Tunable, Redox-Active Diphos Ligands with a Metal-Complex-Backbone

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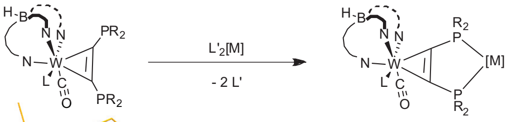
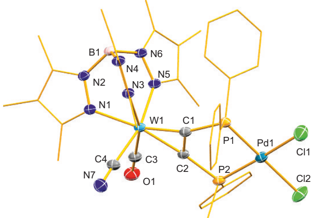
α-P-Substituted Alkyne-Complexes as Ligands





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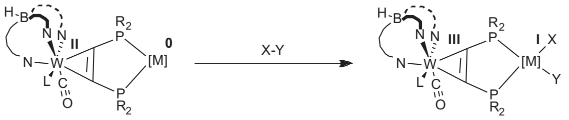
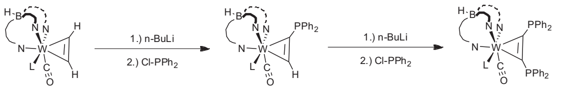
	free ligand **3**	binuclear complex **4**
∠P1C1C2	139.7(9)°	120.2(3)°
∠P2C2C1	134(1)°	119.1(2)°
∠C3W1C4	87.9(2)°	90.5(2)



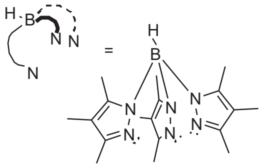
Even though bis(diphenylphosphino)ferrocene and its derivatives have been used in homogeneous catalysis for decades, their intrinsic redox-activity has yet to be incorporated into the catalytic process itself.
Since every cycle usually starts with an oxidative addition to the transition metal in use, it might be advantageous to introduce a ligand that can be oxidized itself.

Thereby, the first row of transition metals, preferring one-electron-oxidations, might be used in catalytic reactions instead of those from the second or third. In such a case, the second electron would be provided by the backbone of the diphos ligand. Possible systems like Cu^0/Cu^I, Cu^I/Cu^{II} are comparatively cheap and Fe^{II}/Fe^{III} even pharmacologically harmless.

P-Functionalization of coordinated C_2H_2



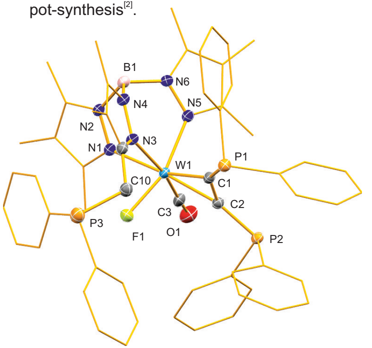
Since bis(diphenylphosphino)acetylene (dppa) tends to coordinate in the end-on-mode, it needs to be created by deprotonation and successive P-functionalization from the corresponding acetylene-complex. Those precursors are generated in a similar way to the ones used by *Templeton* et al.[1].
Depending on the co-ligand L, this process has to be executed stepwise or may be done in a one-pot-synthesis[2].



Hydrido-tris(trimethylpyrazolyl)borate

- tripodal chelating ligand
- usually only spectator in reactions

In the case of L = F, a one-pot-synthesis lead to P-functionalization not only of the alkyne, but also of the Tp*-ligand. This finding can be explained by a weakening of the C-H bond due to a F-H-interaction over a distance of about 200 pm.



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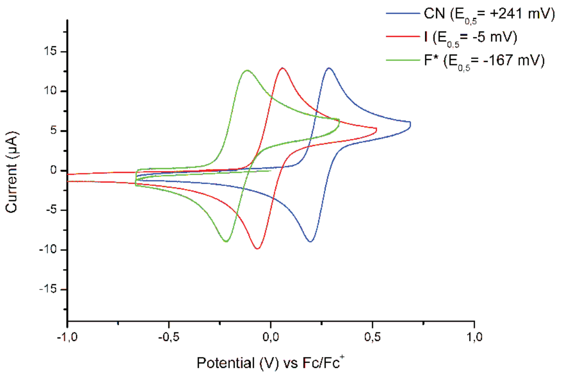
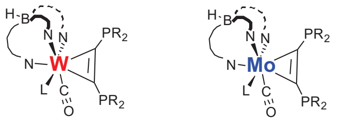
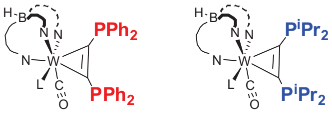
Tuning the Oxidation Potential

Using different co-ligands attached to the metal centre of the presented dppa complexes allows for a range of W^{II}/W^{III} potentials spanning more than 400 mV.
Both the I- and CN-substituted species **2** and **3** are easily accessible and can be prepared on the gram-scale. The F- substituted compound **1** is unstable with regard to oxygen and independently of that decomposes in a matter of days when stored in solution. The thrice P-functionalized moiety **5**, however, may prove to be a promising alternative for the reactions of choice.

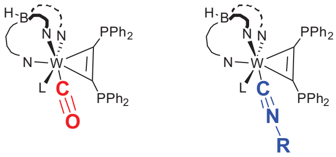




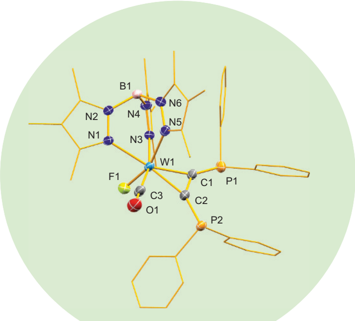
Variations are not limited to the co-ligand attached to the tungsten-centre. As it has been established on similar alkyne-complexes, exchanging tungsten for molybdenum has a significant effect in increasing the M^{II}/M^{III}-oxidation potential by about 150 mV[3].



Smaller changes can be accomplished by variation of the substituents attached to phosphorous. Thereby, the potential of the I-substituted compound **1** (PPh_2) is about 50 mV higher than that of the (P^iPr_2)-analogon.



Furthermore, exchanging the remaining CO-ligand for isonitriles has been realized on (donor-)alkyne-complexes in the past[4] and should represent another way to influence the electrochemical properties of the compounds at hand.



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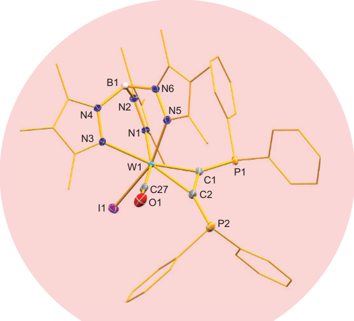

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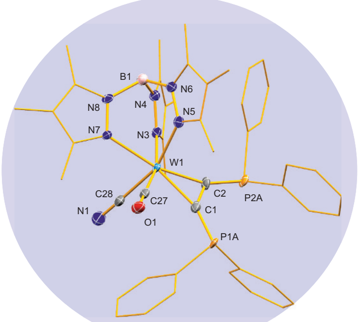

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[1] **J. L. Templeton**, M. B. Wells, P. S. White, *Organometallics* **1997**, *9*, 1857-1864.
[2] **W.W. Seidel**, K. Helmdach, S. Ludwig, A. Villinger, **2016**, *submitted*.
[3] **N. G. Connelly**, C. J. Adams, I. M. Bartlett, S.Carlton, D. J. Harding, O. D. Hayward, A. G. Orpen, E. Patron, C. D. Ray, P. H. Rieger *Dalton Trans.* **2007**, 62-67.
[4] a.) **J. L. Templeton**, A. S. Gamble, S. G. Feng, C. C. Philipp, P. S. White, *Organometallics* **1991**, *10*, 3504-3512.
b.) **W.W. Seidel**, B. L. Sánchez, M. J. Meel, A. Hepp, T. Pape, *Eur. J. Inorg. Chem.*, **2007**, *936-943*.

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