Universität Rostock

Traditio et Innovatio

Synthesis, Coordination Chemistry and Redox Activity of Bidentate W-P,P´ Alkyne Complex-Ligand

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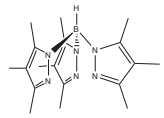
Complex-Ligand Synthesis

Tris(trimethylpyrazolyl)borate:

- anionic
- tripodal
- protected from S_E (unlike Tp´)

Tp* =

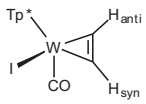


Comments on Synthesis of **3**:

- stepwise synthesis from template
- isolable intermediates
- various substituent combinations possible due to great variety of available electrophiles

Properties and Reactivity of **3**:

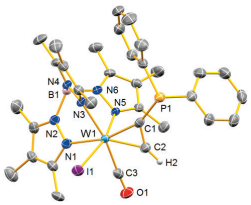
- redox active
- chiral
- air-stable
- soluble in most organic solvents
- reacts readily with a variety of transition metal precursors



1

1) nBuLi
2) ClPPh$_2$

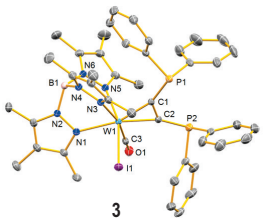
THF



2

1) nBuLi
2) ClPPh$_2$

THF



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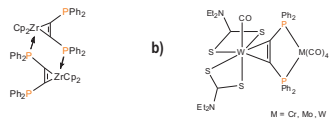
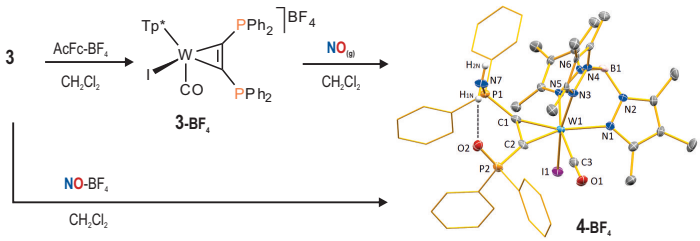


***Fig.* 1** polynuclear complexes with DPPA as bridging ligand

Coordination Chemistry of P Substituted Alkynes:

- dominated by the donor ability of the phosphine functions
- the η^2-*C,C´* binding mode remains rare [I, II]
- only very few published structures for polynuclear complexes with a bridging *C,C´-P,P´* moiety [II, III, IV]
- the $Mo(CO)_4$ building block of complexes **b)** can also be found in our compound **5**

Redoxchemistry and NO Splitting



- one electron oxidation of **3** leads to paramagnetic **3**-BF_4, which is only stable at low temperatures
- the diamagnetic complex **4**-BF_4 forms in a very fast reaction by bubbling NO through a solution of **3**-BF_4
- the unique splitting of NO into its atomic parts is verified by XRD analysis
- no previous activation through coordination at a transition metal is necessary [*cf.* V, VI]
- same product is obtained with NO-BF_4, which serves both as oxidizing agent and NO gas source

Selected bond lenghts [Å]

	3	4-BF_4
W1-C1	2.036(2)	2.036(5)
W1-C2	2.057(2)	2.047(5)
W1-C3	1.966(2)	1.985(6)
C1-C2	1.335(3)	1.322(7)
P1-N7	—	1.609(5)
P2-O2	—	1.487(4)

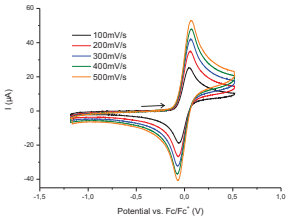


***Fig.* 2** cyclic voltamogramm of **3** at different scan rates

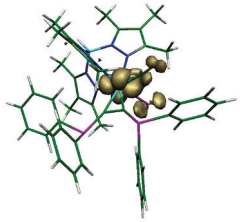
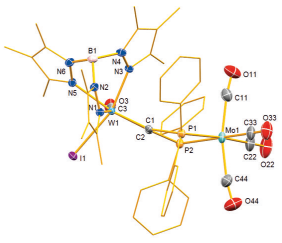


***Fig.* 3** calc. spin density for **3**$^+$ (DFT, ub3lyp)

- reversible oxidation wave at -5 mV (verified by measuring the oxidation wave at different scan rates)
- spin density of **3**$^+$ is located mainly at the tungsten center with some contributions at the iodine and small contributions at the CO moiety
- just very small spin density can be found at the two phosphorus atoms

➔ oxidation is considered to be a W centred redox process

Polynuclear Complexes with Mo(0), Au (I) and Pd(II) - Structures and Cyclic Voltammetry



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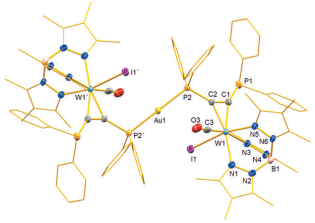
Synthesis:

All three polynuclear complexes were synthesized at room temperature by adding the *P,P´*-alkyne complex **3** to CH_2Cl_2 solutions of $Mo(CO)_4(pip)_2$ yielding **5**, $AuClSMe_2$ and KPF_6 yielding **6**-PF_6 and $(COD)PdCl_2$ yielding **7**.



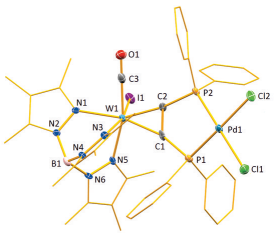
6-PF_6

Coordination of **3**:

- low-field shift for phosphine function(s) in the ^{31}P NMR
- shift of $\nu_{(CO)}$ to higher wave numbers in the IR spectrum

➔ significant loss of electron density at the W^0 center

➔ more positive values for the reversible $W^{II/III}$ redox process



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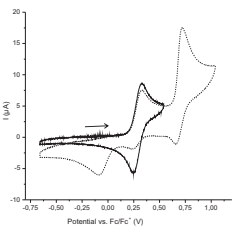
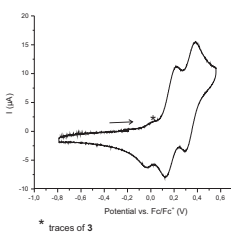


Intramolecular distances [Å] and angles [°]

	3	5	6-PF_6	7
W1-M	—	5.30	4.43	5.05
P1-P2	3.83	3.28	4.06	3.12
C2-C1-P1	133.9	121.3	137.2	118.6
C1-C2-P2	133.71	122.5	141.8	118.7
P1-C1-C2-P2	6.95	13.91	8.05	18.89

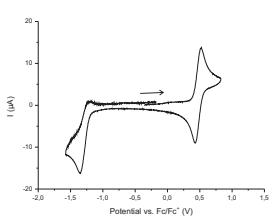


* traces of **3**

^{31}P NMR shifts [ppm] and coupling constants [Hz]

	3	5	6-PF_6	7
δ (P1)	18.12	48.49	15.46	42.86
δ (P2)	20.00	62.23	57.46	56.10
$^2J_{PP}$	11.80	15.61	n.a.	31.21

All cyclic voltamogramms were performed with a glassy carbon working electrode in CH_2Cl_2 solutions containing 0.1M NBu_4PF_6 as supporting elektrolyte. Ferrocene or Acetylferrocene were used as internal standard.



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