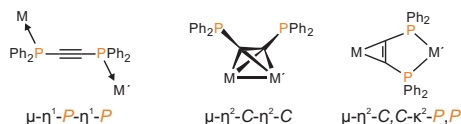


## By A Cationic Bisphosalkyne Complex

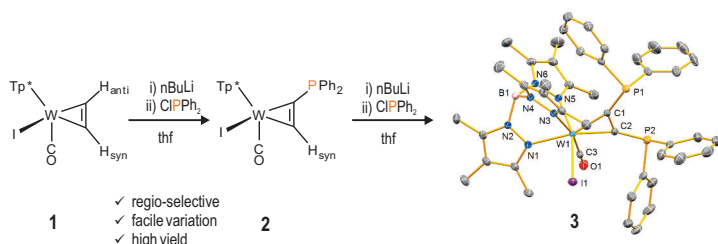
Kai Helmdach (kai.helmdach@uni-rostock.de), Stephan Ludwig, Alexander Villinger and Wolfram W. Seidel\*

### Stepwise Template Synthesis

CSD online search: „dppa“  
130 complex structures  
~ 90 % end-on  
~ 6 % part of TM cluster  
~ 4 % side-on



#### COORDINATION MOTIFS FOR DPPA BRIDGED METAL COMPLEXES<sup>[I-III]</sup>



The slightly modified *Templeton*<sup>[III]</sup> acetylene complex 1 serves as a precursor for the synthesis of bisphosalkyne complexes 3. Stepwise introduction of the functionalities at  $-78^\circ\text{C}$  allows the formation of otherwise unstable electron rich alkynes directly on the metallacyclopropane moiety. Variation of the electrophile, which are not limited to phosphorus chlorides, leads to unsymmetric substituted alkyne complexes.

#### Tris(trimethylpyrazolyl)borate

- anionic
- tripodal chelating ligand
- protected from  $\text{S}_\text{E}$  (unlike  $\text{Tp}^+$ )

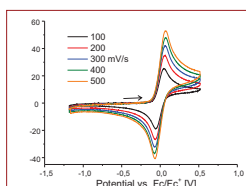
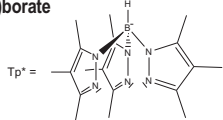
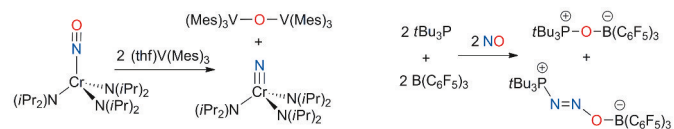


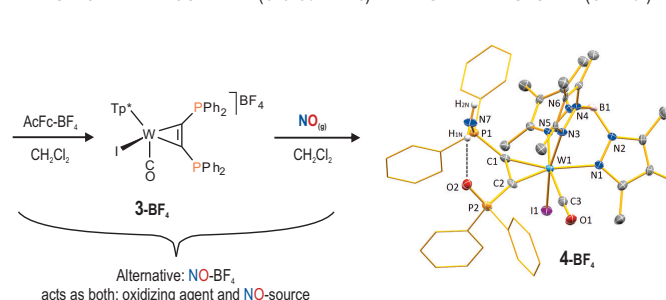
Fig. 1 CV of 3 at different scan rates.

- reversible oxidation wave at  $-5\text{ mV}$
- in situ* IR spectra reveal a strong CO shift from  $1930$  to  $2079\text{ cm}^{-1}$
- $3\text{-BF}_4$  can be crystallized at  $-30^\circ\text{C}$ , otherwise it will disproportionate

### Redoxchemistry and NO Splitting



#### TRANSITION METAL COMPLEX (C.C.Cummins)<sup>[IV]</sup>



#### OPEN FLP SYSTEM (G.Erker)<sup>[V]</sup>

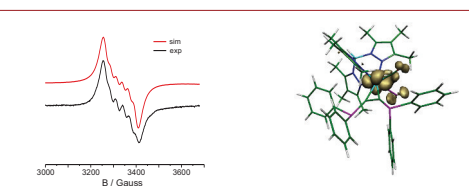
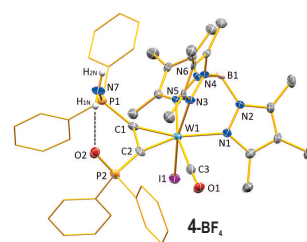


Fig. 2 EPR spectra of  $3^*$  at rt. in  $\text{CH}_2\text{Cl}_2$  / thf.

- EPR shows isotropic signal for  $3^*$  with  $^{101}\text{I}$  (5/2, 100%) hyperfine coupling
- notable absence of  $^{31}\text{P}$  (1/2, 100%) hyperfine coupling
- calculated spin density of  $3^*$  is mainly located at W with some contributions at I and small contributions at CO
- $\rightarrow$  oxidation is considered to be a metal centred redox process ( $\text{W}^{\text{II}} \rightarrow \text{W}^{\text{III}}$ )

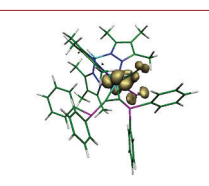


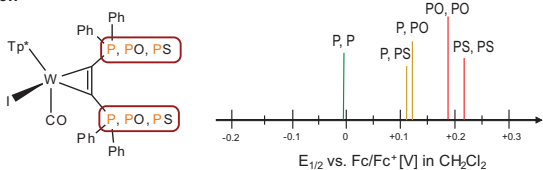
Fig. 3 calc. spin density for  $3^*$  (ub3lyp).

#### Selected bond lengths [Å]

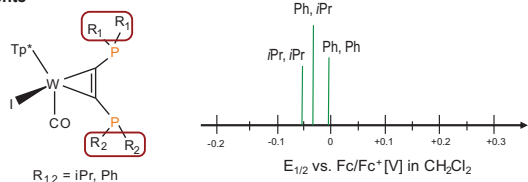
	3	4-BF <sub>4</sub>
W1-C1	2.036(2)	2.036(5)
W1-C2	2.057(2)	2.047(5)
W1-C3	1.966(2)	1.985(5)
W1-I1	2.789(1)	2.774(1)
C1-C2	1.335(3)	1.322(7)
C1-P1	1.790(2)	1.770(5)
C2-P2	1.802(2)	1.825(5)
P1-N7	—	1.609(5)
P2-O2	—	1.487(4)

### Modulation of the Oxidation Potential

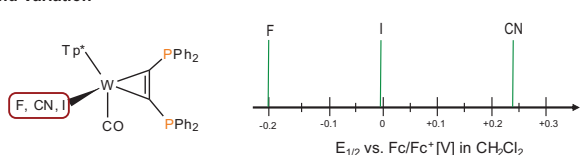
#### P Oxidation



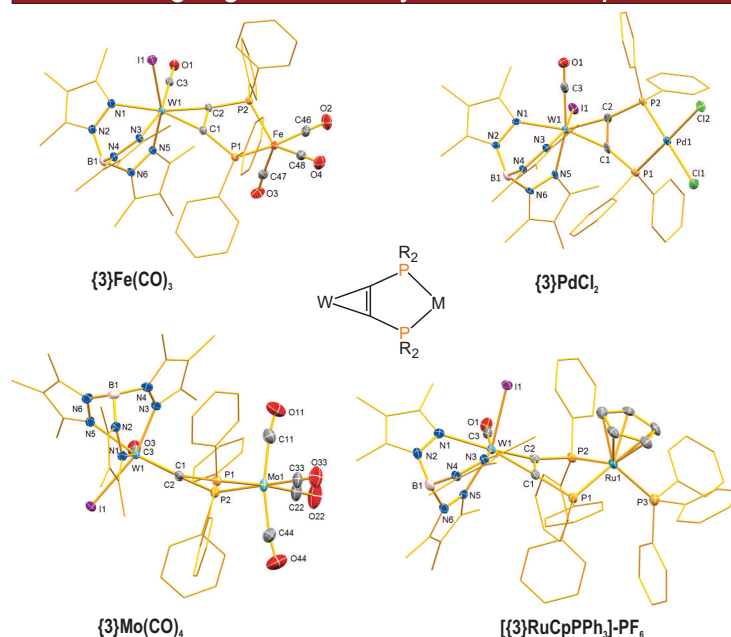
#### P Substituents



#### Ligand Variation



### Chelating Ligand for Polynuclear Complexes



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[II] F.-E. Hong, Y.-C. Chang, R.-E. Chang, S.-C. Chen, B.-T. Ko, *Organometallics* 2002, 5, 961-967.

[III] A. K. Powell, M. J. Went, *J. Chem. Soc., Dalton Trans.* 1992, 3, 439-445.

[IV] M. B. Wells, P. S. White, J. L. Templeton, *Organometallics* 1997, 9, 1857-1864.

[V] A. L. Odom, C. C. Cummins, J. D. Protasiewicz, *J. Am. Chem. Soc.* 1995, 24, 6613-6614.

[VI] A. J. P. Cardenas, B. J. Culotta, T. H. Warren, S. Grimme, A. Stute, R. Fröhlich, G. Kehr, G. Erker, *Angew. Chem. Int. Ed.* 2011, 33, 7567-7571.