Universität Rostock

Traditio et Innovatio

Dual nucleophilic substitution at a dihalogenacetylen-W(II)-complex leading to an amidiniumcarbine

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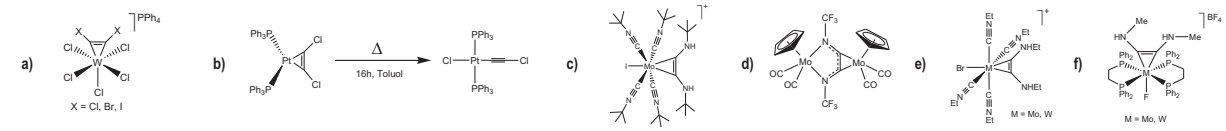
A study on the reactivity of coordinated diiodacetylene towards various nucleophiles

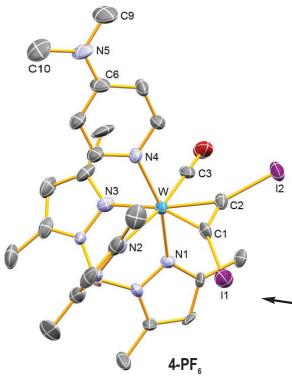
Introduction

With the exception of C_2F_2, dihalogenealkynes are known for over 100 years. Because of their explosive character, coordination chemistry of these alkynes is insufficient explored. Hardly any unequivocal structures are known till today, although their possible potential as a versatile building block for new alkyne complexes is obvious. Nevertheless *Dehnicke* could isolate a number of complexes with a W(IV)-center **a)**, whereas *Suenkel* showed that dihalogenacetylene also tend to form the oxidative addition product **b)**. Nucleophilic Substitution of the halogen could lead to different heterodonor substituted alkyne complexes. The use of amine should result in diaminoacetylene complexes, which are exclusively accessible by coupling two isocyanide ligands at a transition metal center. Some of these compouds are shown below, including examples by *Lippard* **c),** *Lentz* **d)**, *Filippou* **e)** and *Pombeiro et al.* **f)**.



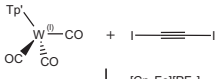
Synthesis and Reactivity of Tp´W(CO)$_2$(η^2-I–C≡C–I)-PF$_6$

Tp´W(CO)$_3$ reacts in the presence of an adequate oxidizing agent with C_2I_2 to form the reactive and unfortunately unstable dicarbonyl alkyne complex **2-PF$_6$**. Prepared *in situ*, it can be transformed into a stable monocarbonyl derivative **4-PF$_6$** using DMAP. Changing the nucleophile to phenylendiamine leads to a new member of tungsten(IV)-imido complexes **5-PF$_6$**.



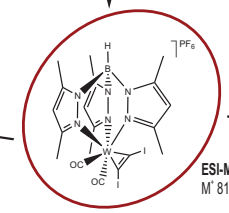
4-PF$_6$

Selected bond lengths [Å] and angles [°]	4-PF6	I–C≡C–I
W-C1	2.02(1)	—
W-C2	2.04(1)	—
C1-C2	1.28(2)	1.19
C1-I1	2.06(1)	1.99
C1-C2-I2	138.9(8)	180



[Cp$_2$Fe][PF$_6$]

Cp$_2$Fe

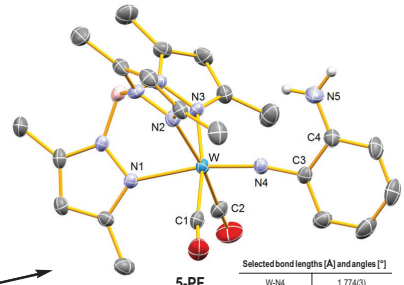


2-PF$_6$

4-Dimethylaminopydridine

Phenylendiamine

ESI-MS:
M$^+$ 815 m/z

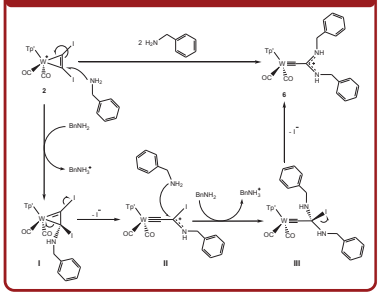


5-PF$_6$

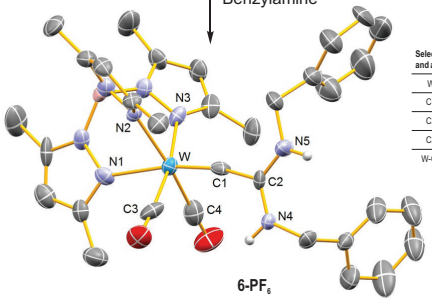
Selected bond lengths [Å] and angles [°]	
W-N4	1.774(3)
N4-C3	1.375(4)
W-N4-C3	168.8(2)

The presented reactions can be monitored by *in-situ* IR-spectroscopy in methylene chloride. The C_2I_2 complex **2-PF$_6$** shows two distinctive CO bands (ν_{CO} 2073; 2006 cm^{-1}) indicating relative weak M-CO bonding. However the spectrum of monocarbonyl species **4-PF$_6$** exhibits only one intense band (ν_{CO} 1948 cm^{-1}) among three new vibration bonds typical for the aromatic DMAP ligand.

Putative mechanism for the formation of 6



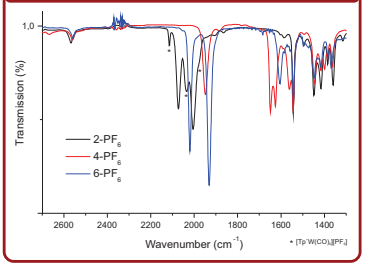
Benzylamine



6-PF$_6$

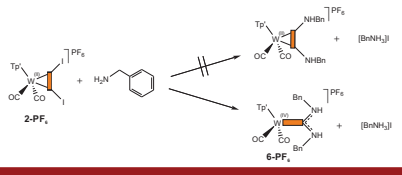
Selected bond lengths [Å] and angles [°]	
W-C1	1.80(1)
C1-C2	1.45(1)
C2-N4	1.32(1)
C2-N5	1.35(2)
W-C1-C2	168.6(8)

Infrared spectra of 2-, 4- and 6-PF$_6$



Conclusion

When **2-PF$_6$** is exposed to an excess of benzylamine, a dual nucleophilic substitution occurs. Surprisingly the η^2-geometry is converted into unique amidiniumcarbine complex **6-PF$_6$** containing both tungsten carbine and cationic amidinium function is formed. This compound is an isomer of the originally intended diaminoacetylene complex. A possible mechanism based on stepwise substitution is presented above. We are currently investigating this mechanism and aiming to isolate one of the suggested intermediates (**I-III**) or to detect them by using *in situ* IR spectroscopy.



In addition to the molecule structure of **6-PF$_6$** spectroscopic data was collected. The IR spectra in solution (DCM) shows two intensive CO bands shifted to lower energies compared to **2-PF$_6$** (ν_{CO} 2020; 1936 cm^{-1}). The NH absorption band is not shown in the picture above, but can be observed at ν_{NH} 3358 cm^{-1}. Unique feature is the presence of a CN valence band (ν_{CN} 1605 cm^{-1}) with average intensity, which is comparable to other amidinium compounds. All bands are in accordance with the results of frequency analysis based on DFT calculations.

[1] K. Stahl, U. Müller, **K. Dehnicke**, Z. *Anorg. Allg. Chem.* **1985**.
K. Stahl, A. El-Kholi, U. Müller, **K. Dehnicke**, J. Organomet. Chem. **1986**.
K. Stahl, F. Weller, **K. Dehnicke**, Z. Anorg. Allg. Chem. **1986**.

[2] **K. Suenkel**, U. Birk, C. Robl, Organometallics **1994**.

[3] C. T. Lam, P. W. R. Corfield, **S. J. Lippard**, J. Am. Chem. Soc. **1977**.

[4] **D. Lentz**, I. Brüdgam, H. Hartl, Angew. Chem. **1984**.

[5] **A. C. Filippou**, W. Grünleitner, Z. Naturforsch. **1991**.

[6] Y. Wang, J. J. R. F. Da Silva, **A. J. L. Pombeiro**, M. A. Pellinghelli, A. Tiripicchio, R. A. Henderson, R. L. Richards, J. Chem. Soc., Dalton Trans. **1995**.

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