New Alkyne Complex Based Framework for Visible Light induced Electron Transfer

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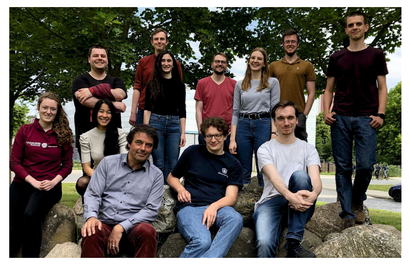


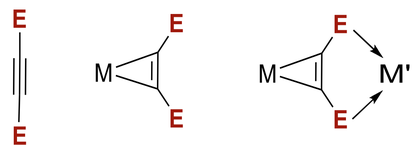
Seidel Group

SPP 2102

Introduction

- W(II)-alkyne complexes bearing donor atoms in both α-positions

→ combines redox-active complex moiety with a potentially chelating unit
→ valuable building blocks for polynuclear compounds with a short metal-metal distance and interesting redox behaviour
→ so far, we were able to form heterobimetallic complexes using C, P, N, S or O as donor atoms [1]

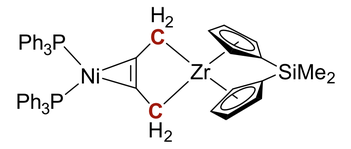


E = C, P, N, S, O

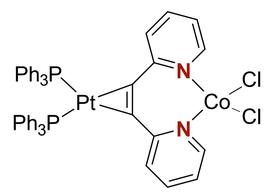
This project

- this project is focused on the new C,N_{py}-donor combination to mimic the phenyl pyridine ligand [2]
- in the literature, only C,C- or N_{py},N_{py}-bridged heterobimetallic alkyne complexes are known [3]

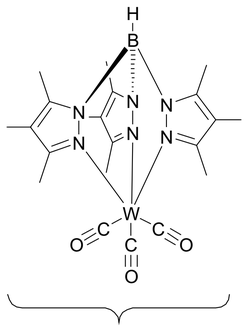
→ within these new complexes the potential light induced electron transfer from the tungsten-centre towards the photocentre is investigated



Rosenthal

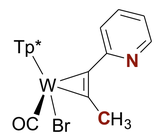


Newkome



$Tp^*W(CO)_3$

1) Py-CC-CH_3, $FcPF_6$
DCM
2) NBu_4Br
THF



1

$\tilde{\nu}$ (CO) = 1906 cm^{-1}

1) $[Ru(bpy)_2(PPh_3)Cl][PF_6]$
2) KO*t*Bu
THF, reflux

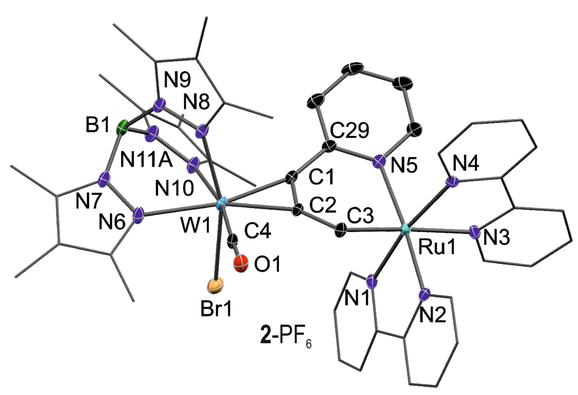
2-PF_6

$\tilde{\nu}$ (CO) = 1893 cm^{-1}

1) $(Ir(ppy)_2Cl)_2$
KO*t*Bu
THF, reflux

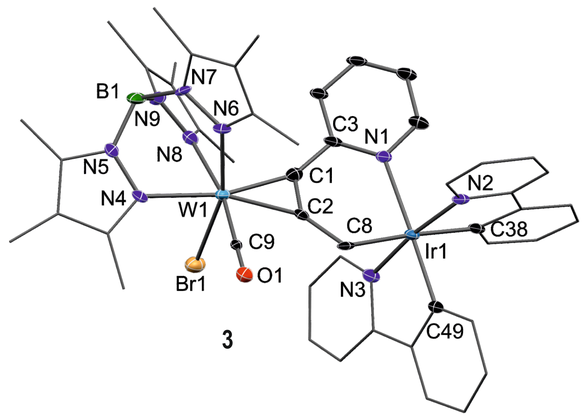
3

$\tilde{\nu}$ (CO) = 1891 cm^{-1}



2-PF_6

Fig. 1: Molecular structure of **2**˙ in the crystal. Selected bond lengths [Å] and angels [°]: W1-C4 1.945(4)), C1-C2 1.323(5), C2-C1-C29 135.7(4), C1-C2-C3 128.2(4), N5-Ru1-C3 94.04(12).



3

Fig. 2: Molecular structure of **3** in the crystal. Selected bond lengths [Å] and angels [°]: W1-C9 1.932(10), C1-C2 1.312(13), Ir1-W1 5.001, C1-C2-C8 137.2(10), C2-C1-C3 128.9(9), N1-Ir1-C8 91.8(3).

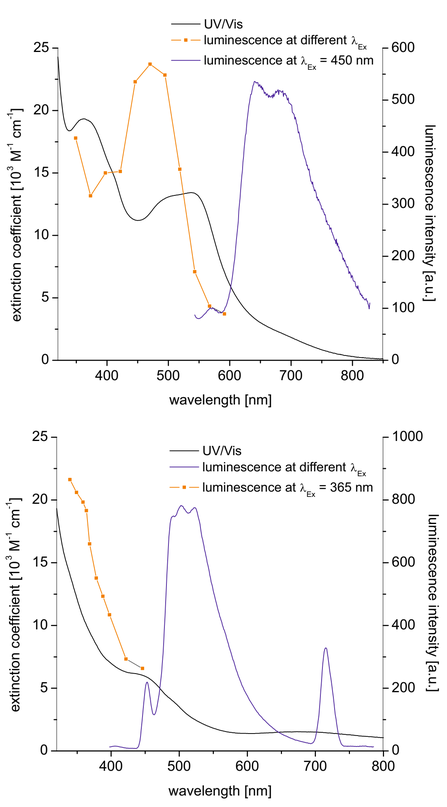


Fig. 3: Absorption spectra at 293 K and luminescence spectra at 77 K of **2**-PF_6 (top) and **3** (bottom).

	Φ [%]
2-PF_6	0.006
3	0.3
$Ir(ppy)_3$	73.0
$[Ru(bpy)_3]^{2+}$	9.5

→ The drastically quenched quantum yields suggest an electron transfer from the W(II) towards the photo-excited metal-centre.

Fig.4: CV measurements of **1**, **2**-PF_6 and **3** in CH_2Cl_2 vs. Fc/Fc^+

oxidation is metal based
1: W-based
2-PF_6 and **3**
1. oxidation W-based
2. oxidation Ru/Ir-based

reduction is ligand based
2-PF_6: bpy-based
3: py-based

	$E_{1/2}$ (Ox) [V]	$E_{1/2}$ (Red) [V]
1	+0.002	
2-PF_6	-0.26; +0.25	-1.42
3	-0.33; +0.22	-1.55

Rehm-Weller equation: redoxpotential for the photo-excited Ir(IV)- or Ru(III)-centre

$E^*_{1/2}$ ($Ru^{III/II}$) = 0.49 V
$E^*_{1/2}$ ($Ir^{IV/III}$) = 0.85 V

→ The electron transfer from W(II) to the photoexcited metal centres is thermodynamically possible.

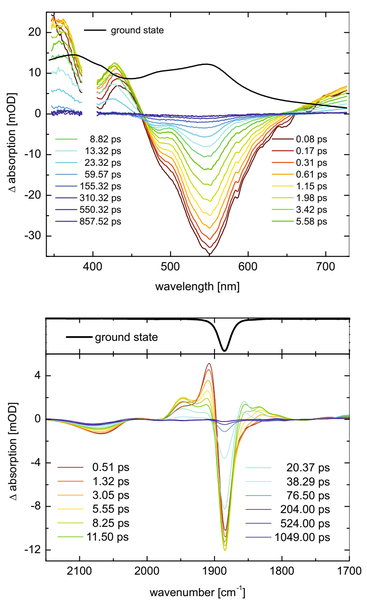
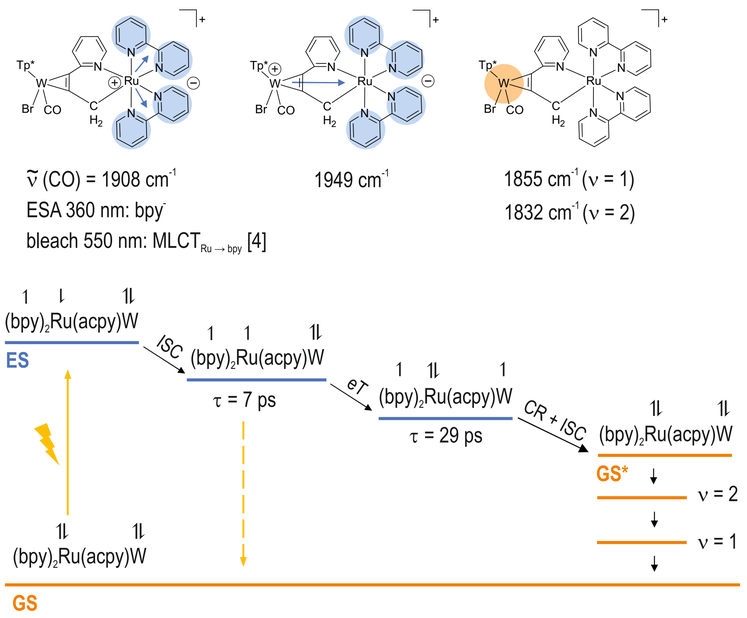


Fig. 5: fs-TA measurements of **2**-PF_6 in CH_3CN; pump pulses at 400 nm; TA-UV/Vis (top) and TA-IR (bottom).



$\tilde{\nu}$ (CO) = 1908 cm^{-1}
ESA 360 nm: bpy^-
bleach 550 nm: $MLCT_{Ru \rightarrow bpy}$ [4]

1949 cm^{-1}

1855 cm^{-1} (ν = 1)
1832 cm^{-1} (ν = 2)

ISC: Intersystem crossig; eT: electron transfer; CR: charge recombination
GS: ground state; ES: excited state

→ The ight induced electron transfer from W(II) towards Ru(III) leads to charge seperated state between the W(III) and the bipyridyle ligand (τ = 29 ps).

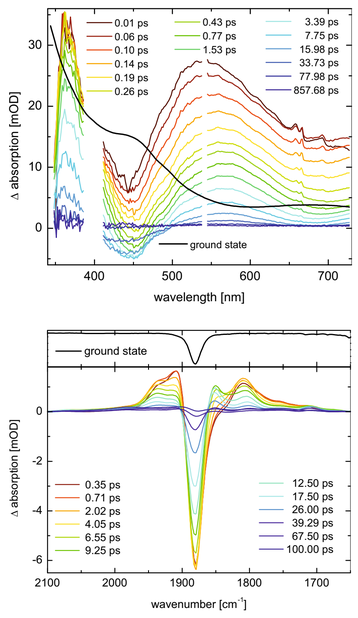
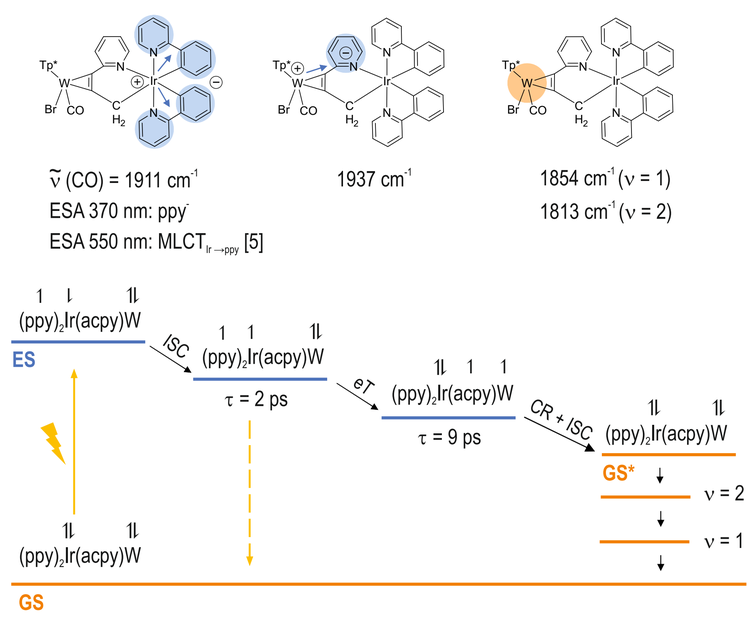


Fig. 6: fs-TA measurements of **3** in CH_3CN; pump pulses at 400 nm; TA-UV/Vis (top) and TA-IR (bottom).



$\tilde{\nu}$ (CO) = 1911 cm^{-1}
ESA 370 nm: ppy^-
ESA 550 nm: $MLCT_{Ir \rightarrow ppy}$ [5]

1937 cm^{-1}

1854 cm^{-1} (ν = 1)
1813 cm^{-1} (ν = 2)

ISC: Intersystem crossig; eT: electron transfer; CR: charge recombination
GS: ground state; ES: excited state

→ The light induced electron transfer from W(II) towards the Ir(IV) leads to a charge seperation between the W(III) and the pyridine ligand (τ = 9 ps).

[1] (a) J. Rüger, C. Timmermann, A. Villinger, W. W. Seidel, *Inorg. Chem.* **2019**, *58*, 9270; (b) K. Helmdach, A. Villinger, W. W. Seidel, *Organometallics* **2017**, *36*, 4844; [2] M. Hüttenschmidt, H. Lange, M. A. A. Cordero, A. Villinger, S. Lochbrunner, W. W. Seidel, *Dalton Trans.* **2022**, *51*, 852; [3] (a) T. Beweries, M. A. Bach, V. V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg, U. Rosenthal, *Organometallics* **2007**, *26*, 241; (b) G. R. Newkome, G. L. McClure, S. F. Watkins, B. Gayle, R. E. Taylor, R. Musselman, *J. Org. Chem.* **1975**, *40*, 3759.

[4] (a) W. Holzer, A. Penzkofer, T. Tsuboi, *Chem. Phys.* **2005**, *308*, 93. (b) K. Suzuki, A. Kobayashi, S. Kaneko, K. Takehira, T. Yoshihara, H. Ishida, Y. Shiina, S. Oishi, S. Tobita, *Phys. Chem. Chem. Phys.* **2009**, *11*, 985. [5] (a) C. M. Elliott, E. J. Hershenhart, *J. Am. Chem. Soc.* **1982**, *104*, 7519. (b) A. N. Tarnovsky, W. Gawelda, M. Johnson, C. Bressler, M. Chergui, *J. Phys. Chem. B* **2006**, *110*, 26497. [6] (a) M. S. Mehata, Y. Yang, Z.-Z. Qu, Chen J.-S., F.-J. Zhao, Han K.-L., *RSC Adv.* **2015**, *5*, 34094. (b) K.-C. Tang, K. L. Liu, I.-C. Chen, *Chem. Phys. Lett.* **2004**, *386*, 437.

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