Universität Rostock

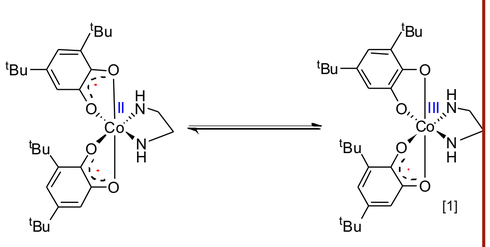
Redox-Isomerism

in a dinculear, donor-alkyne-bridged complex

Stephan Ludwig, Kai Helmdach and Wolfram W. Seidel*

Introduction

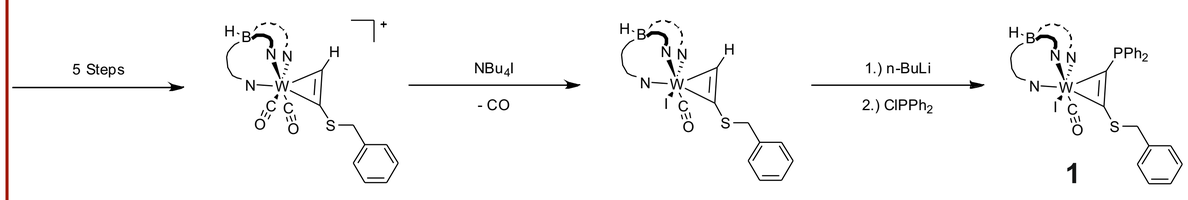
Redox-isomerism has been described[1] in various systems in which an electron is transferred from the metal center of a complex to its redox-active ligand, or vice versa. In contrast to mesomerism, two distinguishable species are observed. Those show different chemical and magnetical properties, even though the conversion rates may be so fast that, on the EPR-timescale, only an average spectrum is obtained.[2] Redox isomers of a compound usually show differences in their structure.



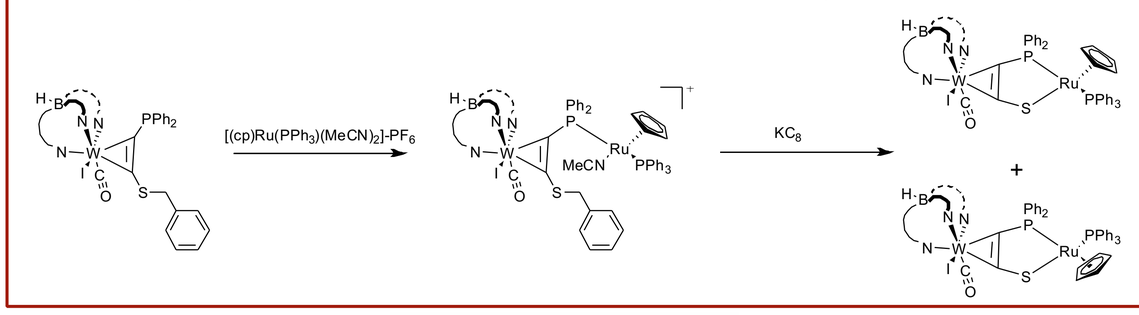
Herein, we present a dinuclear [W-bridge-Ru]-complex which was obtained in two isomeric forms that differ only in the relative arrangement of ligands on the chiral metals. The isomers were seperated, isolated in their pure form and, exploiting their isomerisation at high temperatures, are convertable into each other. Upon oxidation, one isomer shows a W-centered, and the other a Ru-centered redox-process, which has been proven by IR, EPR and visible absorption spectroscopy.

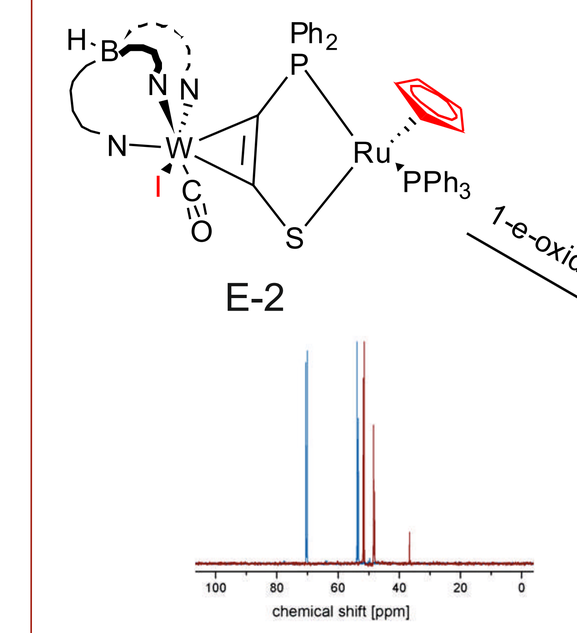
Synthetic Approach

Bis-donor-substituted alkynes are a class of bridging ligands that lead to very short metal-to-metal-distances. However, only a few examples of such compounds, like bis-phosphino-acetylenes, show intrinsic stability and can be isolated in their pure form. Those containing nitrogen-, oxygen- or sulfur-donors often need to be stabilized by protective groups, or built up step-by-step after coordination to a metal center via the triple bond.
In the system presented here, a protected thio-alkyne[3] has been coordinated to a well-established W-complex moiety.[4], leading to a cationic tungsten-alkyne-complex, which is subsequently converted into the mixed-P,S-donor-ligand **1**.

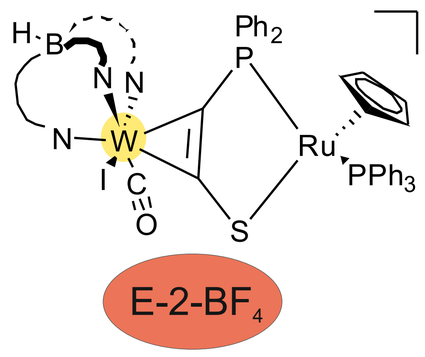


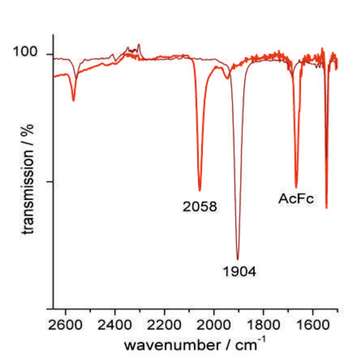
The complex-ligand is treated with a suitable Ru-precursor, which is coordinated via the phosphine-function. Subsequently, the protective benzyle-group at the sulfur-atom is cleaved reductively to give a mixture of **E-2** and **Z-2** in about 25% crystalline yield.

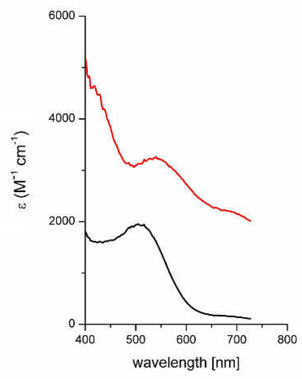


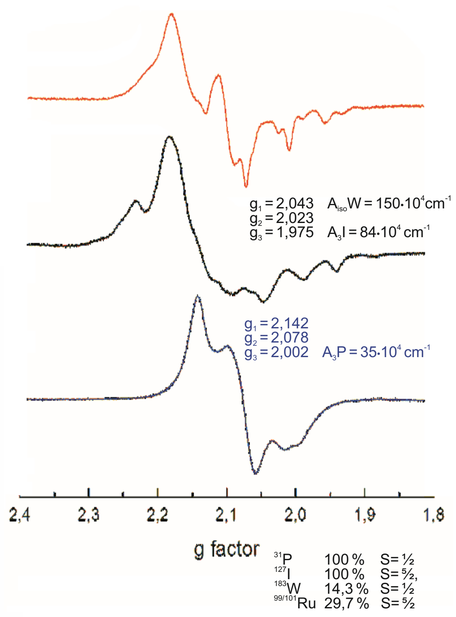


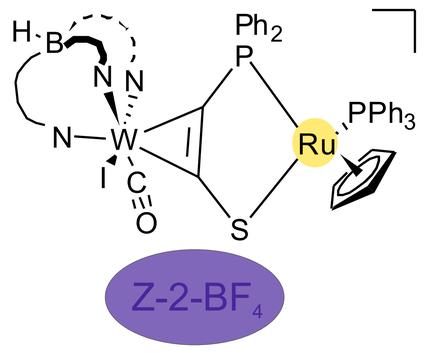
Both isomers show rather different ^{31}P-NMR-shifts for the triphenylphosphine bound to the Ru-center. In contrast, the phosphorous-atom in the donor-alkyne-bridge appears to be largely unaffected by the stereochemistry.
Structural differences have been determined by X-ray-crystallography and are largely characterized by the planarity of the [W-bridge-Ru]-fragment.

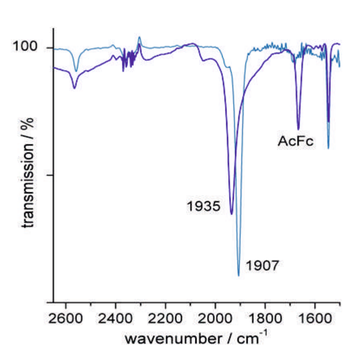


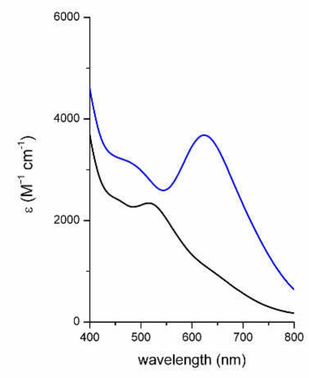


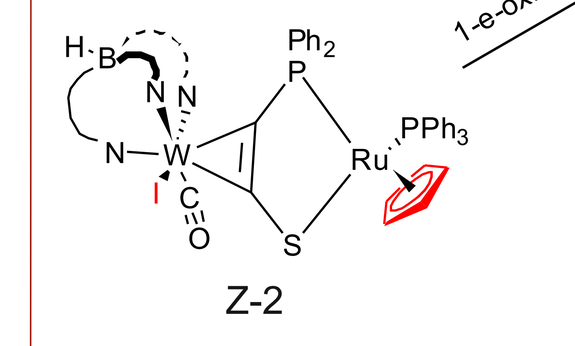










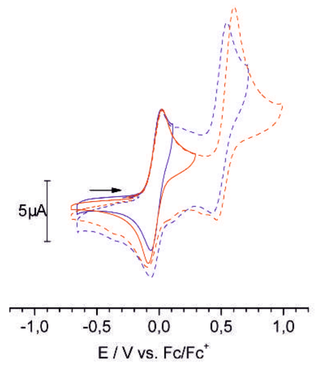


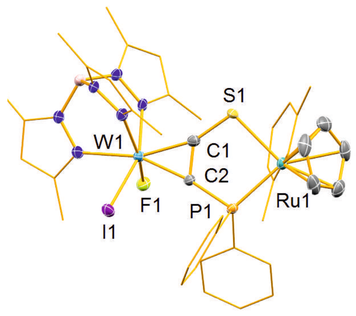
The presence of CO as an infrared-probe allows evaluation of the loss of electron density at W resulting from the oxidation. A W-based oxidation (E-2/ E-2$^+$, red), therefore, leads to a significantly larger increase in wavenumber compared to a Ru-centered oxidation (Z-2/ Z-2$^+$, blue).

The oxidation of both isomers is accompanied by a change in colour from red to a deep green. Visible absorption spectroscopy reveals a far greater change in exitation energy in the Z-isomer (3417 cm^{-1}, blue) than the E-isomer (1284 cm^{-1}, red).

The ESR-spectrum of 1-BF$_4$ (black) reflects a W-based spin density and shows a similar pattern as E-2-BF$_4$ (red). The spectrum of Z-2-BF$_4$ (blue), however, is quite different and indicates a radical centered neither at [W] nor at the ligands.

Cyclic voltammetry reveals both isomers of 2 to show quite similar redox behaviour. A reversible one-electron-oxidation can be observed at about -30 mV for both species. Only the second, far less reversible oxidation, occurs at 600 mV (E-2, red) and 530 mV (Z-2, blue) and supports the assignment of different electronic situations after the first step.





A possible isomerisation and associated change of charge-localization in (E and Z)-2-BF$_4$ at higher temperatures could not be investigated. Both species show decomposition in solution over the course of a few hours above 0°C, though they can be stored for far longer periods of time as a solid. The mechanism involves disproportionation of the W^{III}-species and attack on its BF$_4$-anion under dissociation of CO, the result of which is shown to the left.

[1] a.) **R. M. Buchanan**, C. G. Pierpont, *J. Am. Cem. Soc.*, **1980**, *15*, 4951-4957
b.).**O. Sato**, J. Tao, Y.-Z. Zhang, *Angew. Chem. Int. Ed.* **2007**, *46*, 2152-2187
[2] **H. Grützmacher,** F. F. Puschmann, J. Harmer, D.Stein, H. Rüegger, B. de Bruin, *Angew. Chem. Int. Ed.* **2010**, *49*, 385-389
[3] **W. W. Seidel**, M. J. Meel, M. Schaffrath, T. Pape, *Eur. J. Org. Chem.*, **2007**, 3526-3532
[4] **J. L. Templeton**, C. C. Philipp, P. S. White, *Inorg. Chem.*, **1992**, *31*, 3825-3830.

INSTITUT FÜR CHEMIE| **Universität Rostock,** Albert-Einstein-Straße 3a | 18059 Rostock | Germany