



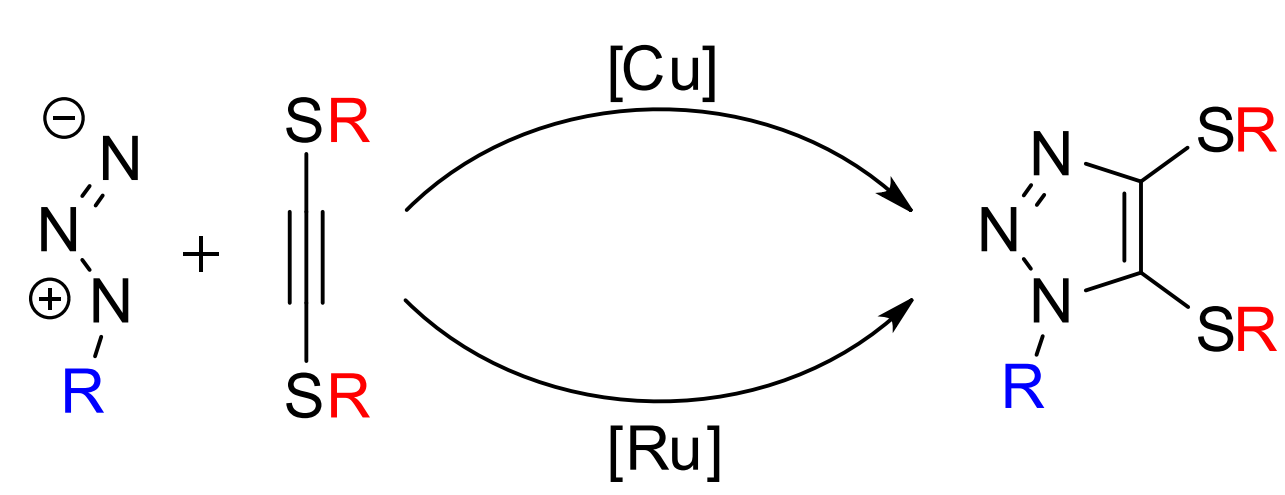
# Structure and Coordination Behaviour of 1*H*-1,2,3-Triazole Ligands with a Dithiolene Backbone

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## Introduction

Dithiolene complexes are well-known for delocalized electronic states, which involve both metal centres and ligands. In conjunction with a multistep redox variability dithiolene complexes represent versatile building blocks for materials with interesting electronic properties.

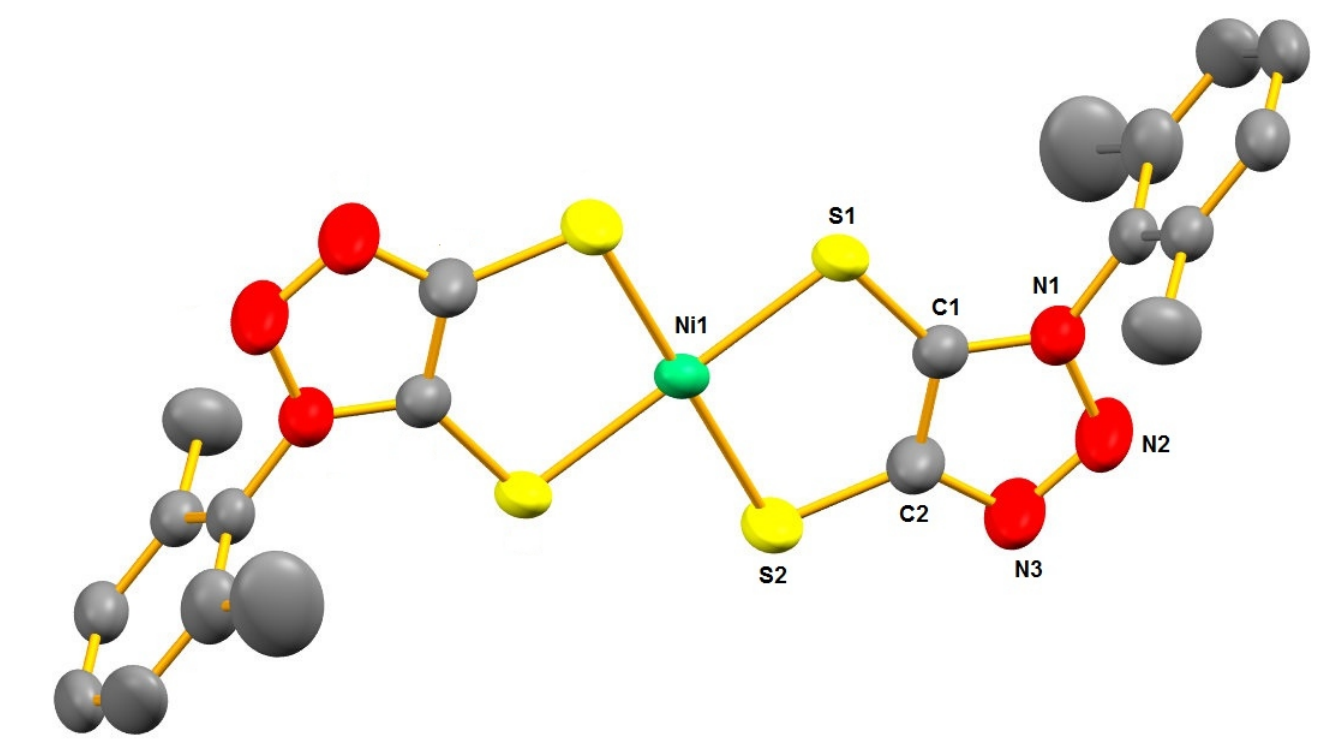
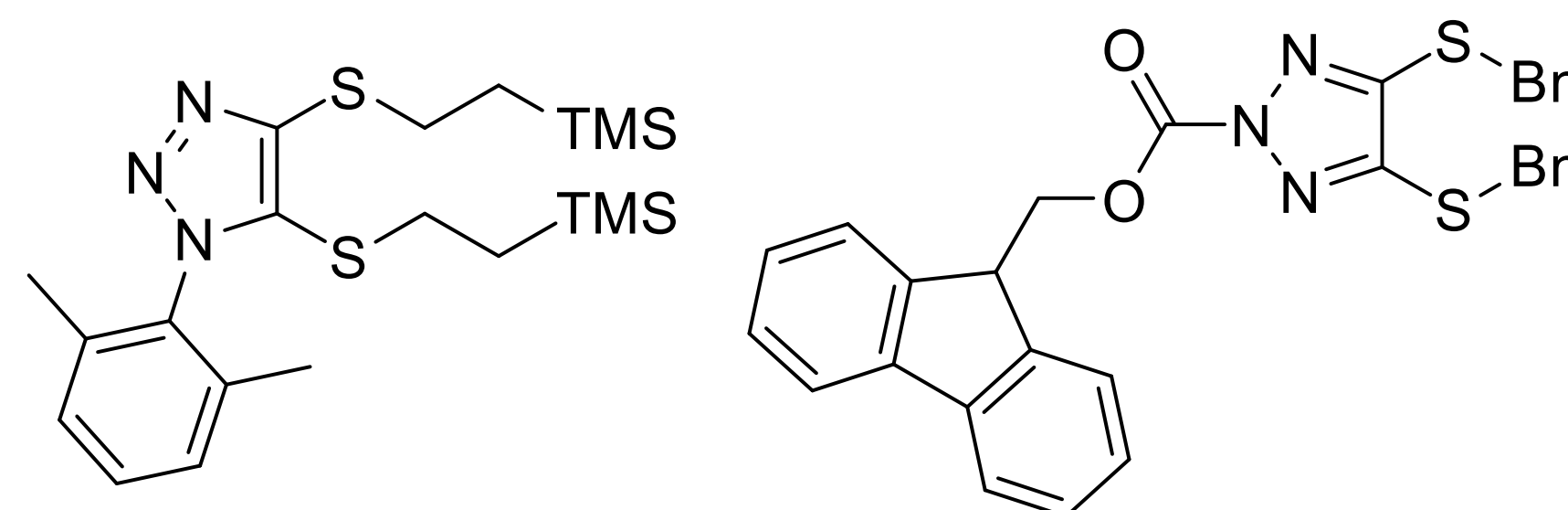
However, the most interacting prototype system with NH-triazole is still missing. The latter would allow the formation of neutral coordination polymers by N-deprotonation and subsequent coordination.



[Cu]: 40 %  
R = DIMP R = Bn  
[Cu]: 27 %  
R = Bn R = TMSE  
[Cu]: 39 %  
R = Bn R = Bn

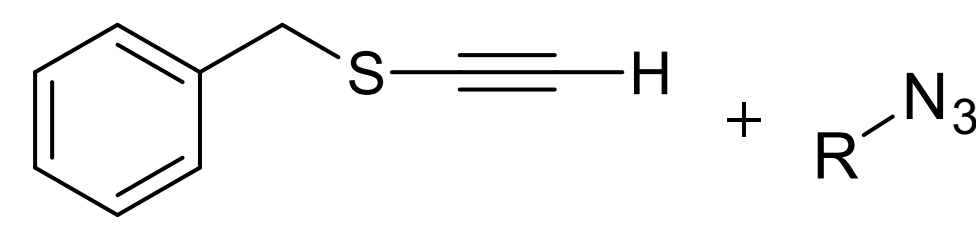
catalyzed by [(NHC)Cu]<sub>2</sub>  
complicated catalyst

Triazole-5,6-dithiolate seems to be a perfect bridging dithiolate ligand, because coordination polymers can be formed by subsequent N-coordination in a very flexible way. First triazole-4,5-dithiolates and their complexes have been prepared by Schallenberg in our research group. [1]



## Results

It was shown that the 4-substituted benzylthio 1*H*-1,2,3-triazole **1** was isolated with very good yields by literature-known copper catalyzed cycloaddition (table 1). [2,7]



CuSO<sub>4</sub>  
Na ascorbate  
K<sub>2</sub>CO<sub>3</sub>

simple catalyst

At 5-position, the second benzylthio group was generated by deprotonation reaction with sulfur and alkylation (**2**).

Starting from R = TMSE, the triazole can be deprotected by TBAF. After protonation, an NH equilibrium of 2*H*- and 1*H*-1,2,3-triazole is established.

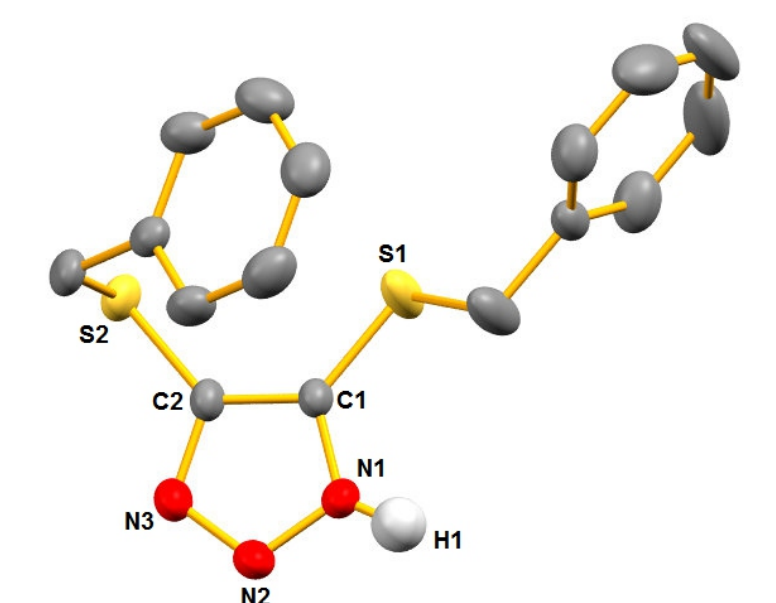
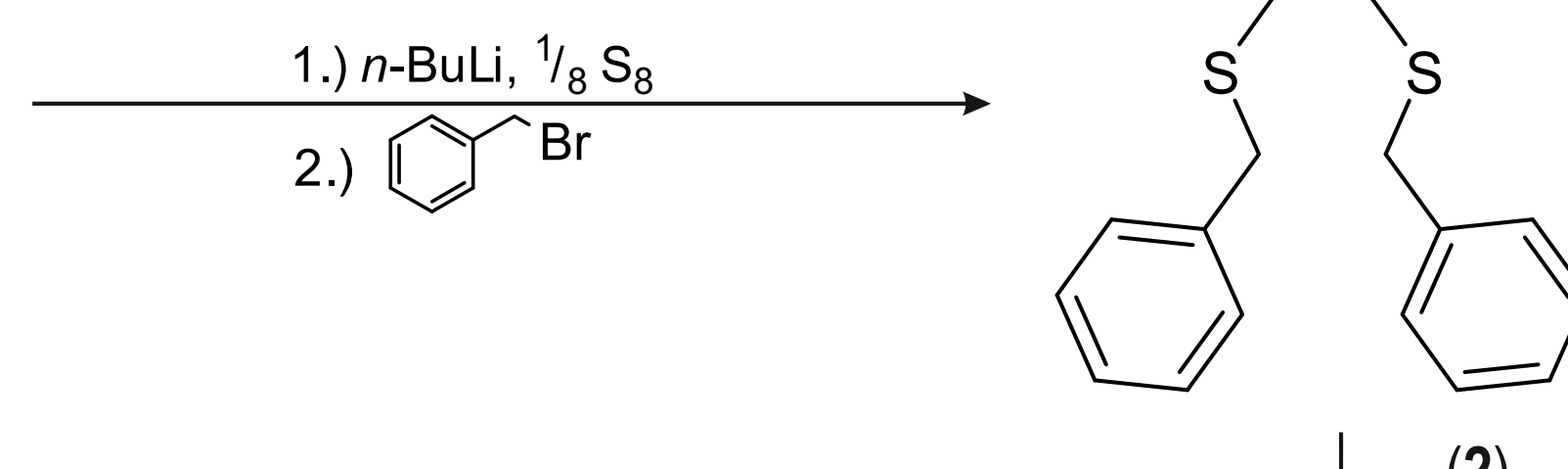
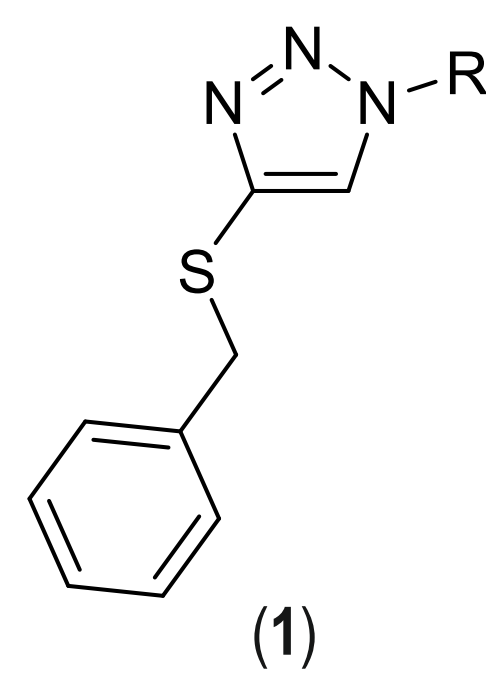
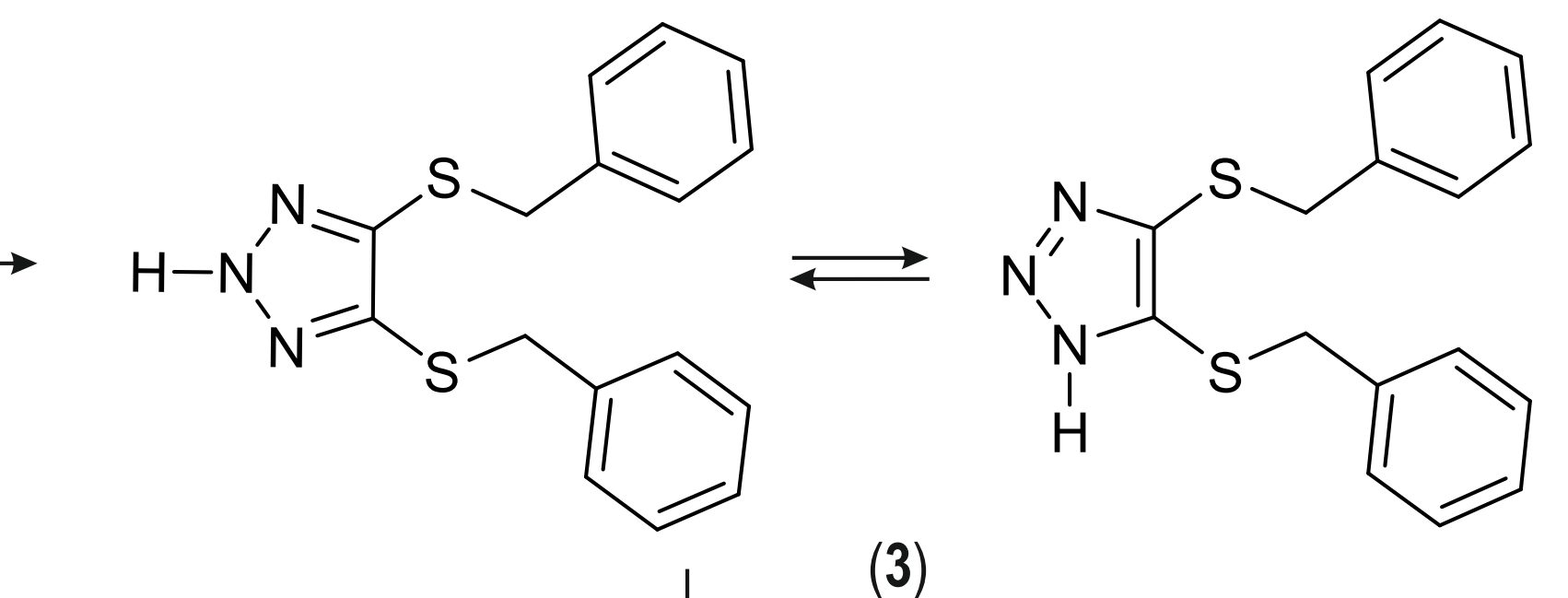


Table 1: The yield of **1** and **2** by different substituents

	<b>1</b>	<b>2</b>
	97%	76%
	76%	89%
	62%	48%

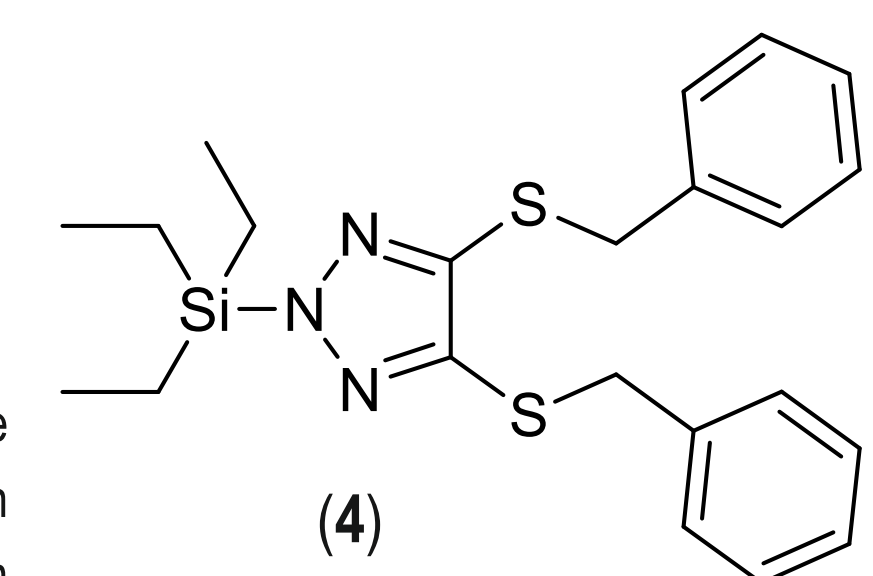


1.) TBAF  
2.) HCl



With Et<sub>3</sub>Si, an orthogonal protective group was introduced, which is particularly easily removed by OH or F sources.

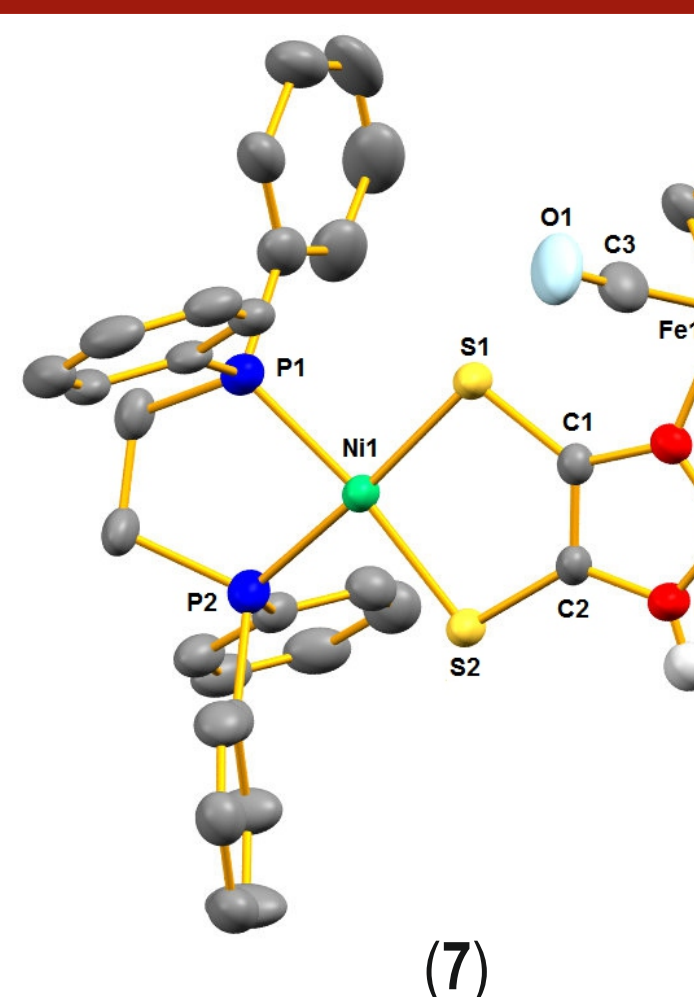
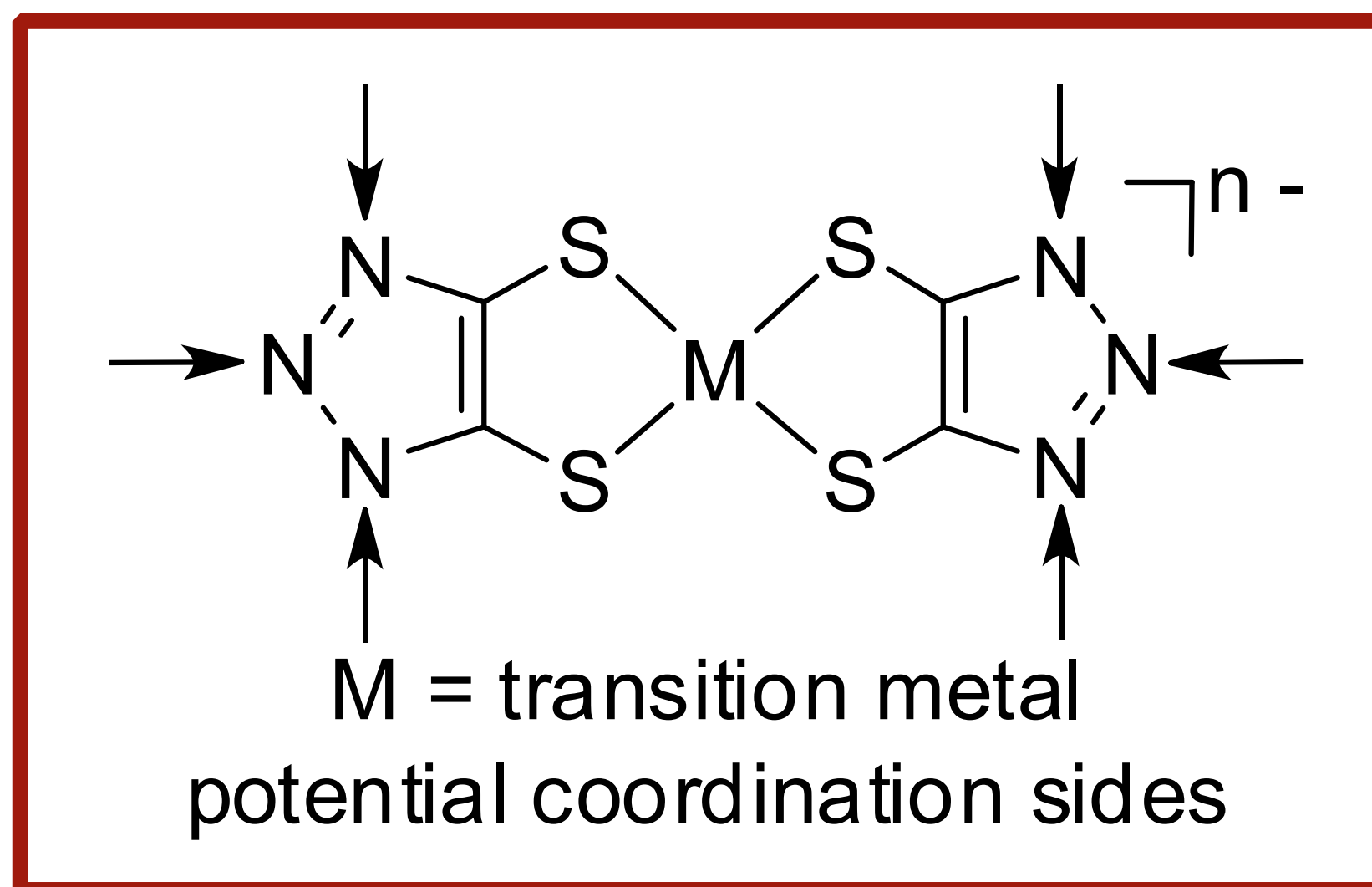
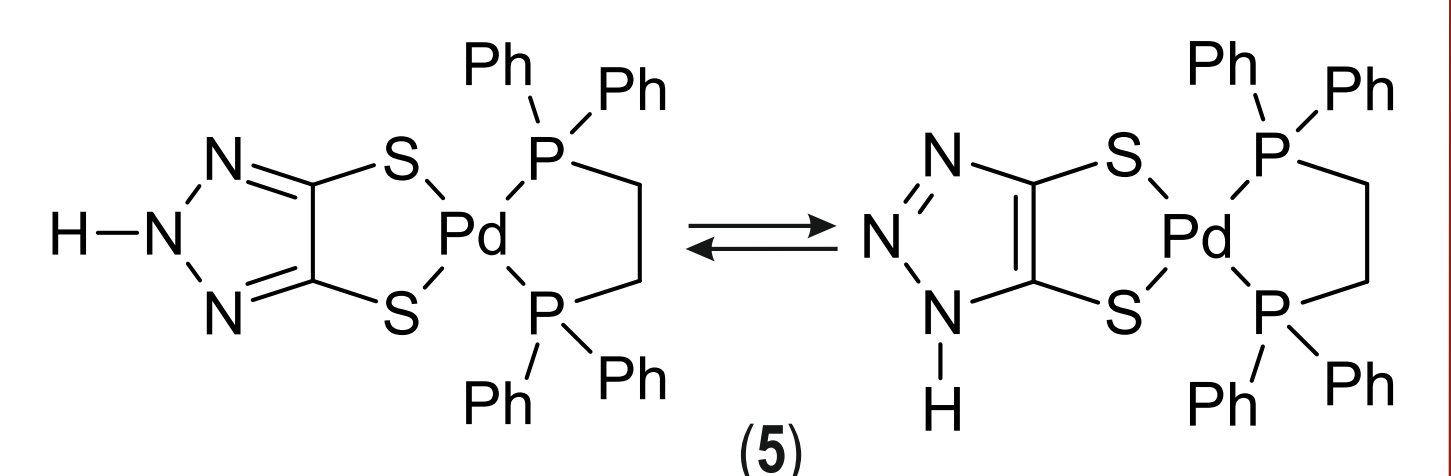
1.) *n*-BuLi  
2.) Et<sub>3</sub>SiCl



Reductive deprotection to the dithiolate moiety allowed an *in situ* coordination with [(dppe)MCl<sub>2</sub>] (M = Ni, Pd) to (**5**) and (**6-H**).

1.) Na,   
2.) KOH, [(dppe)MCl<sub>2</sub>]

Due to the symmetry of crystalline **5**, half of the H-atom lies on the 2*H*- and 1*H*-position, which is interesting for a possible self assembly behaviour in an N-coordination. [5]



C11

(7)

In a reaction of the green amide (**6**) with [CpFe(CO)<sub>2</sub>Br], the first dinuclear complex (**7**) with 1,2,3-triazole-4,5-dithiolate as a bridging ligand could be synthesised.

**5**, **6-H** as well as **7** show an almost planar SCCS moiety, which provides a basis for a good electronic communication via the dithiolene moiety. The longest S1-M1 (M = Ni1, Pd1) bond can be found in **5** due to the atomic radius, while **7** shows a longer S1-Ni1 bond than **6-H** due to the steric nature of [Fe]. [4]

	S1-M1 [Å]	SCCS [°]	N1-Fe [Å]
<b>5</b>	2.3424(6)	-2.7(3)	-
<b>6-H</b>	2.1897(4)	0.00(17)	-
<b>7</b>	2.2005(11)	-6.8(5)	1.956(3)

First electrochemical investigations were carried out on compounds **5** and **6-H**. Here, **5** (red) shows an irrev. reduction (-2.20 V) and oxidation (0.24 V), while **6-H** shows a rev. reduction (-1.81 V) and an irrev. oxidation (0.22 V). **5** and **6-H** show similar properties as the known complexes with 1*H*-protected triazole. [1]

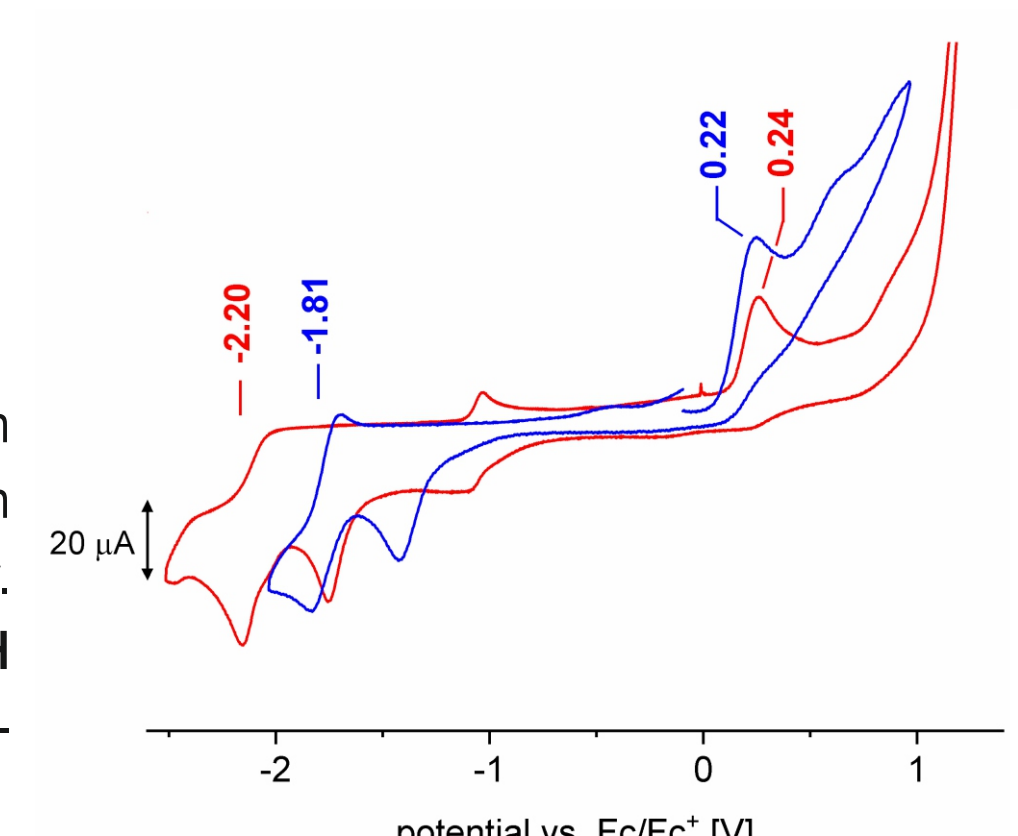


Fig. 2: Cyclic voltammetry of **5** and **6-H** in 0.1 M TBA[PF<sub>6</sub>]-dmf-solution.

After few days, purple crystals could be obtained, which analytically prove a dimerisation to a 18-VE-complex (**9**). [6]

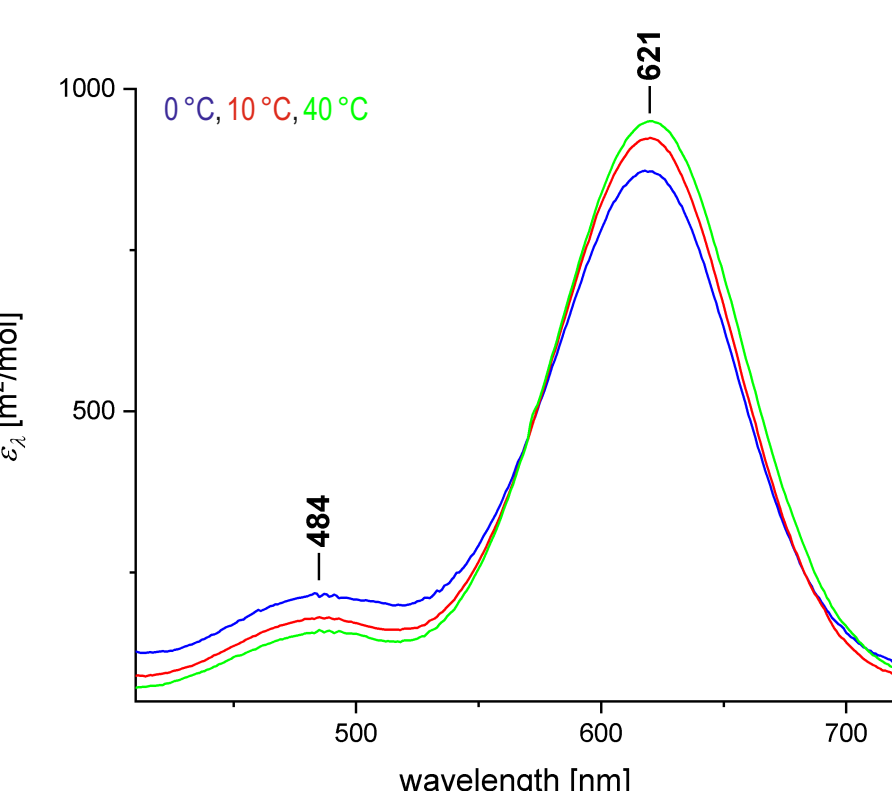


Fig. 1: UV/Vis spectroscopy of **9** in dcm at 0 °C, 10 °C and 40 °C.

Using UV/Vis spectroscopy, a temperature dependent equilibrium between the dimer (484 nm) and the monomer (621 nm) in dcm was uncovered.

[1] D. Schallenberg, PhD thesis, University of Rostock, 2014.

[2] A. S. Kumar, V. D. Ghule, S. Subrahmanyam, A. K. Sahoo, *Chem. Eur. J.*, 2013, **19**, 509-518.

[3] W. W. Seidel, M. J. Meel, M. Schaffrath, T. Pape, *Eur. J. Org. Chem.*, 2007, **21**, 3526-3532.

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[7] N. Pardemann, Msc thesis, University of Rostock, 2021.