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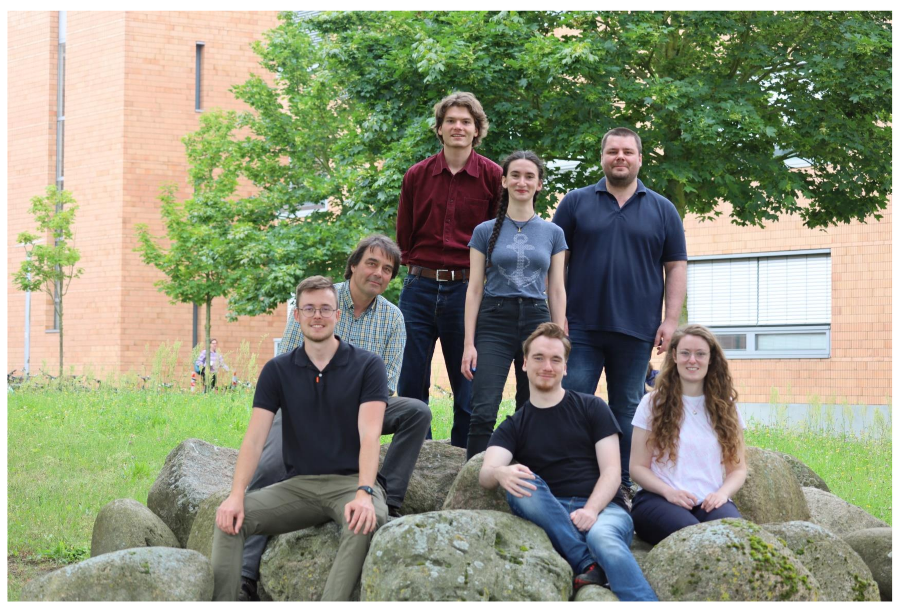
Traditio et Innovatio



Polynuclear complexes with a triazole dithiolate ligand

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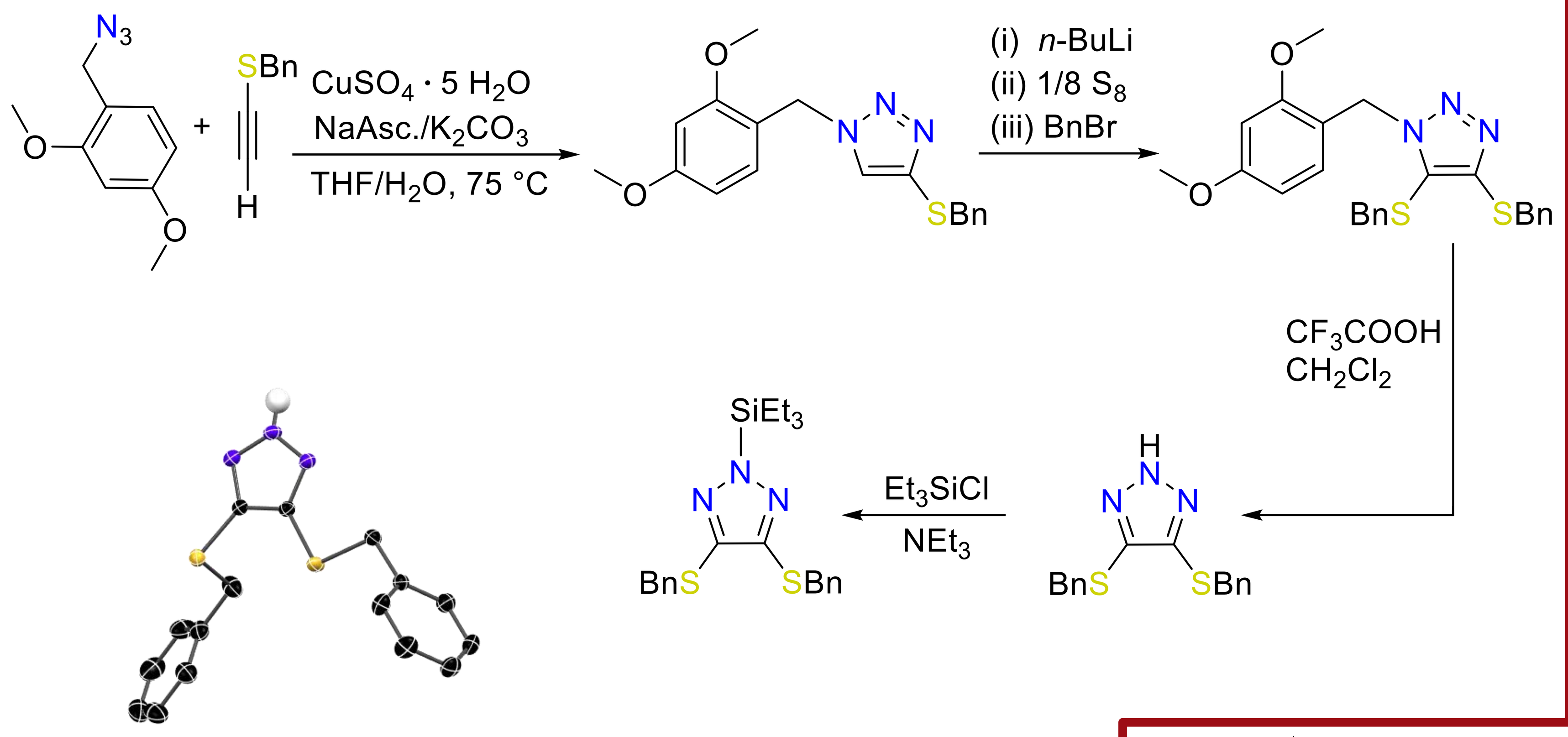
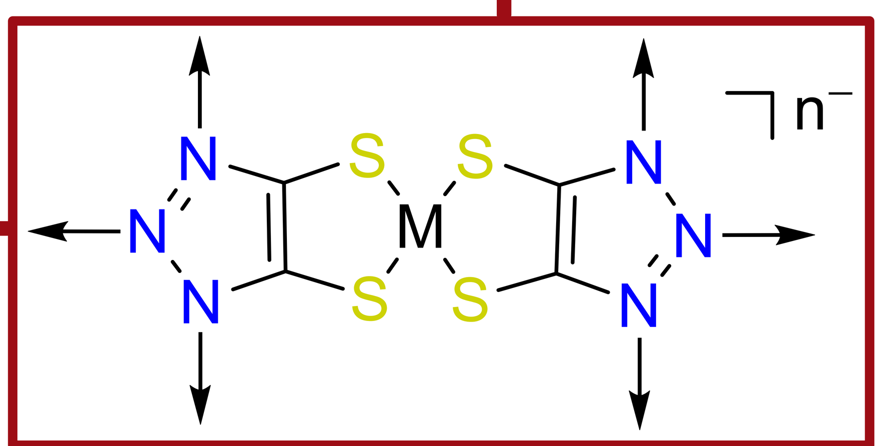
Introduction

Dithiolenes are dithiolate ligands, which are unsaturated in the carbon backbone. The associated delocalisation of electron density renders the sulfur atoms very soft Lewis bases. Combining a dithiolene unit with a triazole creates a versatile ligand, in which the nitrogen atoms serve as relatively hard donors compared to the sulfur centers. However, both sulfur and nitrogen donors can coordinate metal ions, resulting in a variety of different linking modes. Due to the versatility of redox states in dithiolene complexes, transition metal complexes of triazole dithiolate (tzdt^{2-}) are of significant interest in regard to the synthesis of electrically conductive MOFs (Metal-organic framework).

Ligand-synthesis

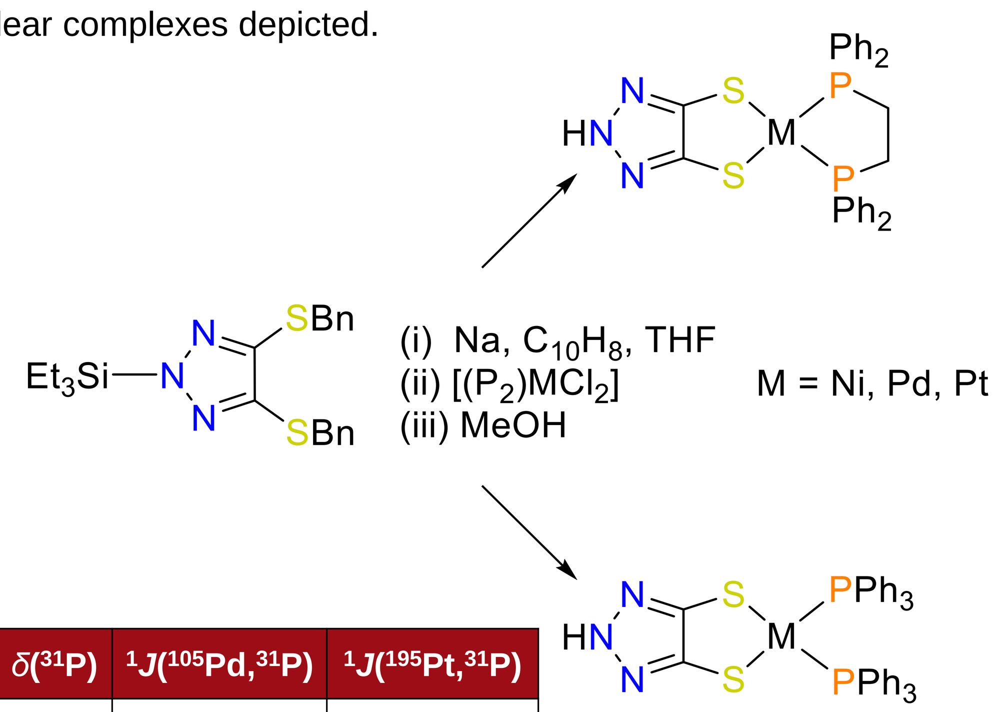
A successful synthesis of the ligand requires orthogonal protective groups. The synthesis begins with an azide-alkyne cycloaddition, in which 2,4-dimethoxybenzyl azide is converted into the corresponding triazole. In the next step, a second sulfur atom must be introduced at the 5-position of the triazole ring to complete the dithiolene unit. Subsequently, the individual protective groups can be selectively removed. The silyl group is cleaved using acids, while the benzyl group can be removed under basic conditions.



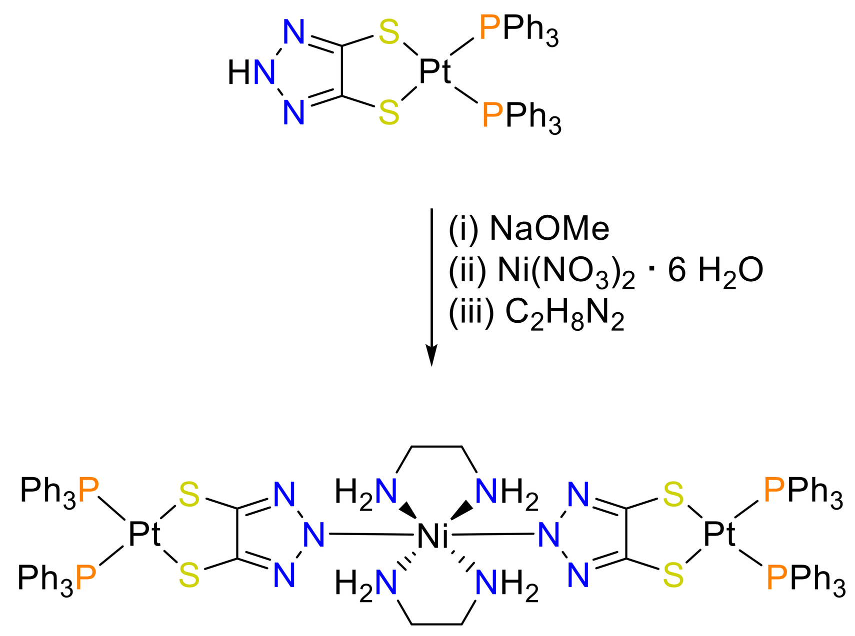


Coordination

Mononuclear complexes can be obtained by reacting various metal precursors with the dithiolene unit. After the triethylsilyl protective group has been attached to the triazole, the benzyl group can be cleaved. This was accomplished by sodium in THF in the presence of naphthalene. Subsequently, coordination of metals like Pd, and Ni led to the monouclear complexes depicted.

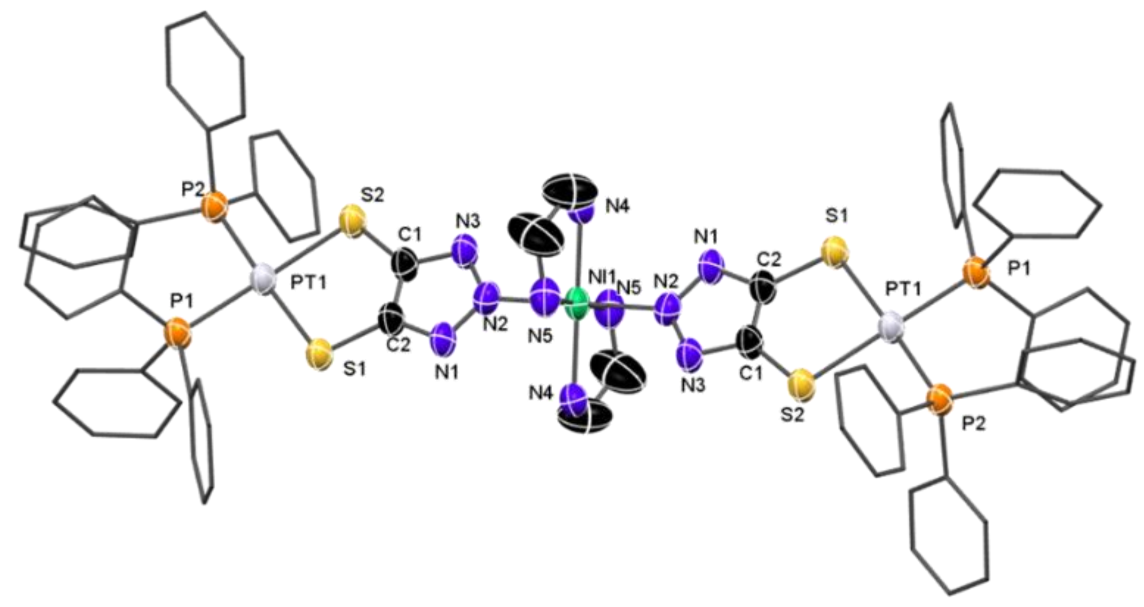


	δ(^{31}P)	^1J(^{105}Pd,^{31}P)	^1J(^{195}Pt,^{31}P)
[(dppe)Ni(tz^{H}dt)]	60.2	-	-
[(dppe)Pd(tz^{H}dt)]	55.4	246 Hz	-
[(PPh_3)$_2$Pt(tz^{H}dt)]	17.1	-	2930 Hz



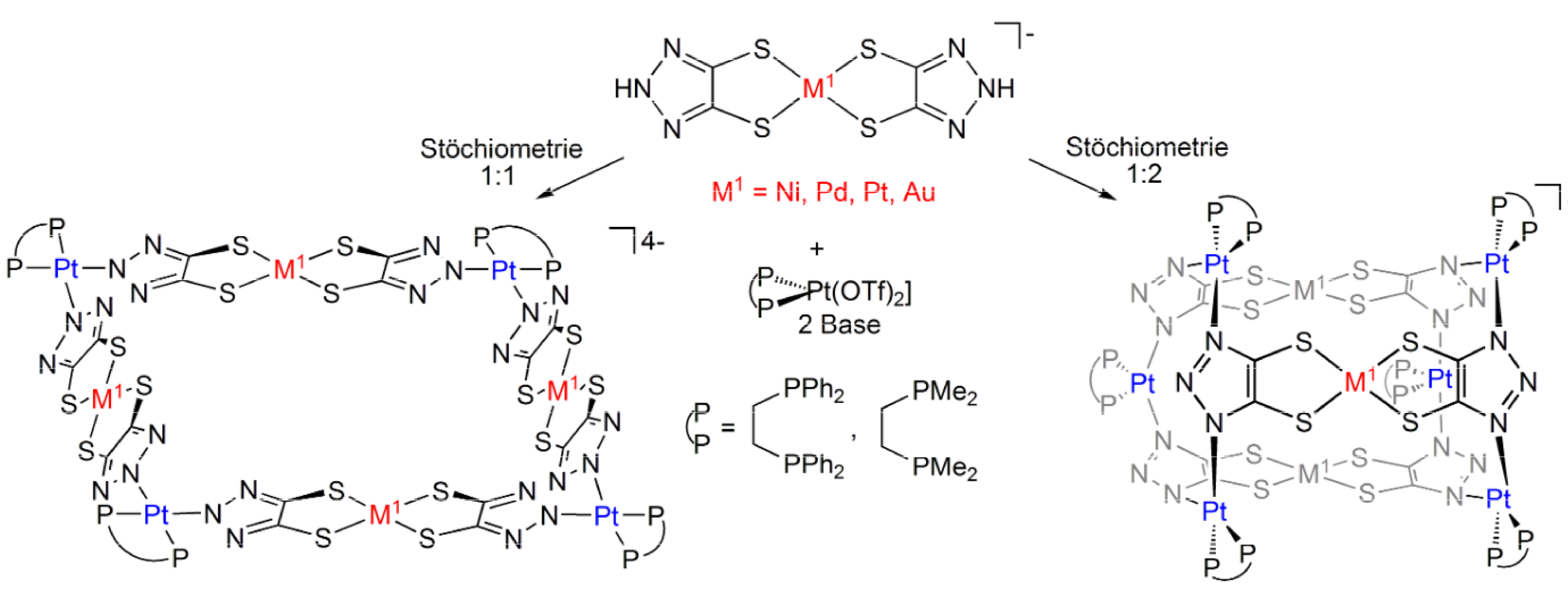
	M-S [Å]
[(dppe)Ni(tz^{H}dt)]	2.1897(4) 2.2006(4)
[(dppe)Pd(tz^{H}dt)]	2.3424(6) 2.3340(6)
[(PPh_3)$_2$Pt(tz^{H}dt)]	2.328(1) 2.352(1)
[Ni(en)$_2${(μ-tzdt)Pt[PPh_3)$_2$}$_2$]	2.3339(2) 2.3411(2)

Subsequent reaction of neutral complexes with nickel(II) nitrate in the presence of ethylenediamine under basic conditions led to the formation of trinuclear complexes, in which the nickel(II) ion is coordinated by two trans-positioned triazole ligands.



Outlook

The triazoldithiolate ligand(tzdt^{2-}) shows significant potential as a bridging ligand for the development of metal-organic frameworks (MOFs). Acting as a linker molecule, tzdt^{2-} can facilitate the formation of complex supramolecular structural motifs. As illustrated in the figure below, these motifs could include square or tubular shapes, offering both stability and versatility. Such supramolecular architectures open up promising applications in fields like catalysis, gas storage, and sensor technology.



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