Improved Synthesis and Coordination Behavior of 1H-1,2,3-Triazole-4,5-dithiolates (tazdt\(^{2–}\)) with Ni\(^{II}\), Pd\(^{II}\), Pt\(^{II}\) and Co\(^{III}\)

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Abstract: A new synthetic route to 1H-1,2,3-triazole-4,5-dithiolates (tazdtH\(^2\)) as ligands for the coordination of Ni\(^{II}\), Pd\(^{II}\), Pt\(^{II}\) and Co\(^{III}\) via the dithiolate unit is presented. Different N-protective groups were introduced with the corresponding azide via a click-like copper-catalyzed azide-alkyne [3 + 2] cycloaddition (CuAAC) and fully characterized by NMR spectroscopy. Possible isomers were isolated and an alternative synthetic route was investigated and discussed. After removal of the benzyl protective groups on sulfur by in situ-generated sodium naphthalide, complexes at the [(dppe)M] (M = Ni, Pd, Pt), [(PPh\(_3\)\(_2\))Pt] and [(η\(^5\)-C\(_5\)H\(_5\))Co] moieties were prepared and structurally characterized by XRD analysis. In this process, the by-products \(11\) and \(12\) as monothiolate derivatives were isolated and structurally characterized as well. With regioselective coordination via the dithiolate unit, the electronic influence of different metals or protective groups at N was investigated and compared spectroscopically by means of UV/Vis spectroscopy and cyclic voltammetry. Complex [(η\(^5\)-C\(_5\)H\(_5\))Co(S)] (10), is subject to a dimerization equilibrium, which was investigated by temperature-dependent NMR and UV/Vis spectroscopy (solution and solid-state). The thermodynamic parameters of the monomer/dimer equilibrium were derived.

Keywords: dithiolene complex; 1,2,3-triazole ligands; click chemistry; CuAAC; thiol protective groups

1. Introduction

The award of the Nobel Prize to Sharpless, Meldal and Bertozzi in 2022 represents an accolade for click chemistry as a powerful synthetic method [1]. The concept of click chemistry was established as early as 2001 and describes a rapid and precise synthesis of molecules following the example of nature. The advantages of the method are high atomic efficiency, very few by-products and high yields while only the use of cheap and simple chemicals and short reaction time are needed [2]. Classically, click chemistry often includes Diels–Alder reactions, addition reactions on carbon–carbon double bonds, and especially copper-catalyzed Huisgen cycloaddition, which can be used for the synthesis of 1H-1,2,3-triazoles [3–5]. Sharpless and coworkers presented first protocols for the [3 + 2] cycloaddition of azides with terminal alkynes under Cu-catalyzed reaction conditions [5]. A [3 + 2] cycloaddition between azides and acetylenes are not regioselective [6–8]. Two regioisomers with a substituent in 4- or 5-position are formed. Only in the case of electrophilically activated acetylenes is high regioselectivity possible [5,9,10]. The copper-catalyzed azide-alkyne [3 + 2] cycloaddition (CuAAC) opens a way for the regioselective synthesis of triazoles. In addition to various alkyl and aryl substituents, donors such as phosphines, amines, sulfur and seleniums could be introduced into the 1H-1,2,3-triazole system as well [11–16]. Introduction of thiol groups at both 4- and 5-position of the triazole would result in a new ligand with five potential coordination sites in the form of the dithiolene unit and the N atoms. Both through the aromatic properties of the 1H-1,2,3-triazole ring and through the specific electronic situation of the dithiolene unit, the 1H-1,2,3-triazole-4,5-dithiolate (tazdt\(^{2–}\)) could serve as a versatile...
bridging ligand between several metal centers. In particular, the electronic properties appear potentially interesting due to the non-innocent character of the dithiolene unit [17–19]. In contrast to many other triazoles, a synthesis of 1H-1,2,3-triazole-4,5-dithiols by means of a click-like copper-catalyzed azide-alkyne [3 + 2] cycloaddition is not known to the best of our knowledge. So far, synthesis of 1H-1,2,3-triazole-4,5-disulfides was reported in a Ru-catalyzed [3 + 2] cycloaddition of an azide and a bis(alkylsulfanyl) acetylene at high temperatures under inert gas atmosphere [16,20]. Alternatively, this synthesis can be carried out with [(NHC)CuI] (NHC = 1-benzyl-3-n-butyl-1H-benz[d]imidazolylidene) as catalyst. The latter is easier to use, but the yields are lower compared with the Ru-based catalyst. In addition, 1H-1,2,3-triazoles have been synthesized in an Ir-catalyzed [3 + 2] cycloaddition of internal mono(alkylsulfanyl)alkynes with an azide [21]. Herein, we present a substantially improved synthesis of 1H-1,2,3-triazole-4,5-disulfides under CuAAC click conditions using the terminal benzylsulfanylacetylene. Pitfalls of the reductive removal of S-protective benzyl groups are identified by isolation of respective thiolato complexes. Finally, we describe coordination of the corresponding dithiols to group 10 metals and CoIII. The influence of the metal and the N-protective groups at the triazole on the electronic properties will be discussed.

2. Materials and Methods

2.1. Chemical Reagents and Instruments

Materials, details on physical measurements, X-ray determination data, original NMR and IR spectra of all products and preparative procedures as well as spectroscopic data of the only organic products (1–4) are provided in the ESI.

2.2. Synthetic Protocols

2.2.1. General Synthesis of 5

A solution of 2a–c (1 mmol) in THF (50 mL) was treated with sodium (5 mmol) and naphthalene (2.5 mmol). The red-brown suspension was stirred overnight, then cooled to 0 °C. MeOH (10 mL) was added and the mixture was stirred until gas evolution ceased. For purification, the solution was dried in vacuo, taken up in H2O (40 mL) and washed three times with Et2O (10 mL aliquots). The aqueous fraction was filtered over celite in a G3 frit and subsequently acidified with aqueous HCl (pH = 3–4), leading to the formation of a beige precipitate. The suspension was extracted four times with CH2Cl2 (aliquots of 10 mL). The organic fraction was dried over Na2SO4, filtered and dried in vacuo to isolate 5 as crude products. According to NMR, the samples are not analytically but sufficiently pure for successful complex synthesis. Potential by-products were characterized in the form of stable complexes as well (see compounds 11 and 12).

H2-5a, 1.049 g (2.42 mmol) 2a, 0.284 g (12.35 mmol) sodium, 0.777 g (6.06 mmol) naphthalene: yield 0.174 g (28%, crude product). 1H NMR (CDCl3, δ, ppm, 300 MHz, 298 K): 7.25–7.22 (m, 2 H, H-o-(4-MOB)), 6.92–6.89 (m, 2 H, H-m-(4-MOB)), 5.45 (s, 2 H, NCH2), 3.81 (s, 3 H, CH3) + additional by-product signals. IR (CH2Cl2, ν, cm−1): 3686 (m), 2978 (s), 2873 (s), 2362 (w), 1604 (m), 1510 (m), 1384 (m), 1274 (s), 1110 (s), 763 (s), 697 (s).

H2-5b, 0.649 g (1.401 mmol) 2b, 0.165 g (7.174 mmol) sodium, 0.834 g (6.507 mmol) naphthalene: yield 0.323 g (40%, crude product). 1H NMR (CD2Cl2, δ, ppm, 300 MHz, 298 K): 7.20–7.17 (m, 1 H, H-(2,4-dMOB)), 6.68–6.62 (m, 2 H, H-m-(2,4-dMOB)), 5.56 (s, 2 H, NCH2), 3.82 (s, 3 H, CH3), 3.79 (s, 3 H, CH3) + additional by-product signals. IR (CH2Cl2, ν, cm−1): 3686 (m), 2978 (s), 2873 (s), 2362 (w), 1604 (m), 1510 (m), 1384 (m), 1274 (s), 763 (s), 697 (s).

H2-5c, 0.632 g (1.53 mmol) 2c, 0.173 g (7.52 mmol) sodium, 0.496 g (3.87 mmol) naphthalene: yield 0.356 g (76%, crude product). 1H NMR (THF-D8, δ, ppm, 300 MHz, 298 K): 4.57–4.31 (m, 2 H, NCH2), 1.32–1.18 (m, 2 H, CH2TMS), 0.07 (s, 9 H, CH3-TMS) + additional by-product signals.
2.2.2. General Synthesis of the Metal Complexes 6 and 7

In a 50 mL flask 1 equivalent [(dppe)MCl2] (M = Ni, Pd) was suspended in 15 mL H2O. A solution of 1.1 equivalents 5b in CH2Cl2 (25 mL) and 3 equivalents KOH were subsequently added. In the two-phase system, a color change from red to green (Ni) or colorless to violet (Pd) was observed in the lower phase. The reaction system was stirred for 3 days at room temperature. To purify the product, the aqueous phase was removed and the organic fraction washed four times with H2O (15 mL), dried over Na2SO4 and filtered and the solvent was removed in vacuo. A column chromatographic purification was carried out with a CH2Cl2/MeOH solvent mixture (20/1) as a mobile phase. Suitable crystals for X-ray structure analysis were obtained from a CH2Cl2 solution by slow diffusion of n-pentane.

[(dppe)Ni(5b)] (6), 0.115 g (0.22 mmol) [(dppe)NiCl2], 0.077 g (1.37 mmol) KOH, 0.068 g (approx. 0.24 mmol) 5b: yield, 0.086 g (54%). Anal. Calcd. for C37H35NiO2NiP2S2: C, 60.18; H, 4.78; N, 5.69; S, 8.68%. Found: C, 59.79; H, 4.71; N, 5.77; S, 8.57%. 1H NMR (CDCl3, δ, ppm, 300 MHz, 298 K): 7.83–7.75 (m, 8 H, -(2,4-dMOB)), 7.52–7.43 (m, 12 H, H-Ph), 6.93 (dd, JH-HH = 8.4 Hz, 1 H, H-o-(2,4-dMOB)), 6.49 (dd, JH-HH = 8.4 Hz, 1 H, H-m’-(2,4-dMOB)), 5.82 (dd, JH-HH = 8.3 Hz, 1 H, H-Ph), 131.6 (s, C-(2,4-dMOB)), 55.3 (s, C-(2,4-dMOB)), 45.5 (s, C-(2,4-dMOB)), 27.5–26.8 (m, CH2-dppe). 31P NMR (CDCl3, δ, ppm, 122 MHz, 298 K): 60.5 (d, JPP = 47.9 Hz, P-dppe), 58.7 (d, JPP = 47.9 Hz, P-dppe). IR (CH2Cl2, ν, cm−1): 2963 (w), 1614 (m), 1508 (m), 1437 (m), 1285 (m), 1103 (m), 739 (s), 691 (m), 532 (m).

[(dppe)Pd(5b)] (7), 0.161 g (0.28 mmol) [(dppe)PdCl2], 0.055 g (0.98 mmol) KOH, 0.084 g (approx. 0.30 mmol) 5b: yield 0.097 g (44%). 1H NMR (DMF-D7, δ, ppm, 300 MHz, 298 K): 8.03–7.87 (m, 8 H, H-Ph), 7.66–7.61 (m, 12 H, H-Ph), 6.88 (dd, JH-HH = 8.4 Hz, 1 H, H-o-(2,4-dMOB)), 6.60 (d, JH-HH = 2.3 Hz, 1 H, H-m’-(2,4-dMOB)), 6.49 (dd, JH-HH = 8.4 Hz, 1 H, H-Ph), 131.6 (s, C-(2,4-dMOB)), 130.7–129.9 (m, C-(2,4-dMOB)), 5.17 (s, 2 H, NCH2), 3.83 (s, 6 H, CH3), 3.03–2.86 (m, 4 H, CH2-dppe). 13C NMR (DMF-D7, δ, ppm, 75 MHz, 298 K): 160.9 (s, C-(2,4-dMOB)), 158.0 (s, C-(2,4-dMOB)), 154.5 (dd, JCP = 10.8 Hz, JCP = 3.9 Hz, C-tazdt), 143.3 (dd, JCP = 12.3 Hz, JCP = 3.7 Hz, C-tazdt), 133.9 (dd, JCP = 11.4 Hz, JCP = 7.0 Hz, C-Ph), 129.7 (d, JCP = 2.4 Hz, C-Ph), 129.4 (s, C-(2,4-dMOB)), 129.3 (dd, JCP = 10.7 Hz, JCP = 7.3 Hz, C-Ph), 117.3 (s, C-(2,4-dMOB)), 104.8 (s, C-(2,4-dMOB)), 98.4 (s, C-(2,4-dMOB)), 55.6 (s, CH3), 55.3 (s, CH3), 44.6 (s, NCH2), 28.2–27.5 (m, CH2-dppe). 31P NMR (DMF-D7, δ, ppm, 122 MHz, 298 K): 58.4 (d, JPP = 18.0 Hz, P-dppe), 56.1 (d, JPP = 18.0 Hz, P-dppe). MS (ESI-TOF, 9:1 MeOH:H2O with 0.1% HCOOH, m/z): 786 (M + H+) . IR (CH2Cl2, ν, cm−1): 3043 (w), 1647 (m), 1437 (m), 1259 (s), 739 (s), 705 (s).

2.2.3. Synthesis of [(dppe)Pt(5b)] (8)

In a 50 mL Schlenk flask [(dppe)PtCl2] (0.088 g, 1.326 mmol) was dissolved in MeOH (10 mL). A solution of 5b (0.042 g, approx. 1.484 mmol) and KOH (0.017 g, 0.303 mmol) in MeOH (10 mL) was added. The yellow suspension was diluted with CH2Cl2 (15 mL) and stirred for 3 days at room temperature. After drying in vacuo the purification was carried out chromatographically with a CH2Cl2/MeOH solvent mixture (20/1) as mobile phase. Crystals suitable for X-ray structural analysis were obtained from a saturated CH2Cl2 solution with n-pentane: yield 0.088 g (75%). 1H NMR (CD2Cl2, δ, ppm, 300 MHz, 298 K): 7.85–7.75 (m, 8 H, H-Ph), 7.52–7.49 (m, 12 H, H-Ph), 6.87 (dd, JH-HH = 8.3 Hz, 1 H, H-o-(2,4-dMOB)), 6.40 (d, JH-HH = 2.4 Hz, 1 H, H-m’-(2,4-dMOB)), 6.33 (dd, JH-HH = 8.3 Hz, 1 H, H-Ph), 4.78; N, 5.69; S, 8.68%. Found: C, 59.79; H, 4.71; N, 5.77; S, 8.57%. 1H NMR (CD2Cl2, δ, ppm, 300 MHz, 298 K): 160.1 (s, C-(2,4-dMOB)), 158.3 (s, C-(2,4-dMOB)), 134.0 (dd, JCP = 11.0 Hz, JCP = 1.1 Hz, C-Ph), 132.3–132.2 (m, C-Ph), 130.0 (s, C-(2,4-dMOB)), 129.2 (dd, JCP = 11.0 Hz, JCP = 2.4 Hz, C-Ph), 117.3 (s, C-(2,4-dMOB)), 104.5 (s, C-(2,4-dMOB)), 98.6 (s, C-(2,4-dMOB)), 55.8 (s, CH3),
In a 50 mL Schlenk flask 1 equivalent [(PPh₃)₂PtCl₂] was suspended in MeOH (10 mL). A solution of 1.1 equivalents 5a-c and 3 equivalents NaOMe in MeOH (10 mL) and CH₂Cl₂ (10 mL) was added. After stirring for 3 days at room temperature, the yellow solution was dried in vacuo and purified by column chromatography with CH₂Cl₂/MeOH solvent mixture (20/1) as mobile phase. Crystals suitable for X-ray structural analysis were obtained from a saturated CH₂Cl₂ solution with n-pentane.

[(PPh₃)₂Pt(5a)] (9a) and (12), 0.207 g (0.26 mmol) [(PPh₃)₂PtCl₂], 0.034 g (0.63 mmol) NaOMe, 0.074 g (approx. 0.30 mmol) 5a: yield 0.088 g (76%, 9a), 12 could be isolated from the first fraction of the same chromatography. ¹H NMR (CD₂Cl₂, δ, ppm, 500 MHz, 298 K): 7.50–7.47 (m, 13 H, H-Ph), 7.38–7.35 (m, 4 H, H-Ph), 7.24–7.18 (m, 13 H, H-Ph), 7.10 (d, ³J_H,H = 8.7 Hz, 2 H, H-O-(4-MOB)), 6.76 (d, ³J_H,H = 8.7 Hz, 2 H, H-m-(4-MOB)), 4.99 (s, 2 H, NCH₂), 3.78 (s, 3 H, CH₃). ¹³C NMR (CD₂Cl₂, δ, ppm, 125 MHz, 298 K): 159.7 (s, C-(4-MOB)), 154.5 (d, ²J_C,P = 8.8 Hz, C-tadtd), 142.7 (d, ³J_C,P = 12.0 Hz, C-tadtd), 135.4 (dd, ³J_C,P = 8.3 Hz, J_C,P = 1.9 Hz, C-Ph), 131.2 (dd, ³J_C,P = 3.6 Hz, J_C,P = 1.9 Hz, C-Ph), 130.4 (s, C-(4-MOB)) 130.3 (dd, ³J_C,P = 9.0 Hz, J_C,P = 9.2 Hz, C-Ph), 128.1 (dd, ³J_C,P = 11.1 Hz, J_C,P = 4.5 Hz, C-Ph), 114.0 (s, C-(4-MOB)), 55.6 (s, CH₃), 51.0 (s, C₂H₆). ³¹P NMR (CD₂Cl₂, δ, ppm, 202 MHz, 298 K): 17.2 (d, ²J_P,P = 21.0 Hz, P-dppe, Pt-satellites: dd, ³J_P,P = 2914.9 Hz, ¼J_P,P = 20.8 Hz), 17.1 (d, ³J_P,P = 21.0 Hz, P-dppe, Pt-satellites: dd, ¹J_P,P = 2943.3 Hz, ³J_P,P = 20.8 Hz). IR (CH₂Cl₂, ν, cm⁻¹): 1436 (m), 1259 (s), 1094 (m), 738 (s), 708 (s), 525 (m).

[(PPh₃)₂Pt(5b)] (9b), 0.192 g (0.24 mmol) [(PPh₃)₂PtCl₂], 0.046 g (0.85 mmol) NaOMe, 0.069 g (approx. 0.24 mmol) 5b: yield 0.103 g (42%). Anal. Calcd. for C₃₇H₄₁N₂O₂Pt₂Si₂: C, 56.39; H, 4.13; N, 4.20; S, 6.41%. Found: C, 56.66; H, 4.27; N, 4.27; S, 6.63%. ¹H NMR (CD₂Cl₂, δ, ppm, 500 MHz, 298 K): 7.53–7.43 (m, 12 H, H-Ph), 7.38–7.34 (m, 6 H, H-Ph), 7.23–7.18 (m, 12 H, H-Ph), 6.86 (dd, ³J_H,H = 7.98 Hz, J_H,H = 0.56 Hz, 1 H, H-O-(2,4-dMOB)), 6.36 (t, ³J_H,H = 2.41 Hz, 1 H, H-Ph), 6.33 (d, ³J_H,H = 2.41 Hz, 1 H, H-Ph), 5.03 (s, 2 H, NCH₂), 3.78 (s, 3 H, CH₃), 3.65 (s, 3 H, CH₃). ¹³C NMR (CD₂Cl₂, δ, ppm, 125 MHz, 298 K): 161.0 (s, C-(2,4-dMOB)), 158.5 (s, C-(2,4-dMOB)), 154.2 (dd, ³J_C,P = 14.2 Hz, J_C,P = 3.2 Hz, C-tadtd), 143.3 (dd, ³J_C,P = 16.0 Hz, J_C,P = 3.6 Hz, C-tadtd), 135.4 (t, ²J_C,P = 10.8 Hz, C-Ph), 131.2 (dd, ³J_C,P = 12.3 Hz, J_C,P = 2.4 Hz, C-Ph), 130.8 (s, C-(2,4-dMOB)), 130.4 (dd, ³J_C,P = 56.4 Hz, J_C,P = 29.3 Hz, J_C,P = 1.7 Hz, C-Ph), 128.1 (dd, ³J_C,P = 11.1 Hz, C-Ph), 117.0 (s, C-(2,4-dMOB)), 104.5 (s, C-(2,4-dMOB)), 98.5 (s, C-(2,4-dMOB)), 55.8 (s, CH₃), 55.7 (s, CH₃), 45.5 (s, NCH₂). ³¹P NMR (CD₂Cl₂, δ, ppm, 202 MHz, 298 K): 17.7 (d, ²J_P,P = 21.0 Hz, P-dppe, Pt-satellites: dd, ¹J_P,P = 2996.7 Hz, ³J_P,P = 20.8 Hz), 16.7 (d, ³J_P,P = 21.0 Hz, P-dppe, Pt-satellites: dd, ¹J_P,P = 2835.2 Hz, ³J_P,P = 20.8 Hz). IR (CH₂Cl₂, ν, cm⁻¹): 3055 (m), 1437 (m), 1268 (s), 1094 (w), 738 (s), 710 (s), 526 (m).

[(PPh₃)₂Pt(5c)] (9c), 0.260 g (0.33 mmol) [(PPh₃)₂PtCl₂], 0.067 g (1.24 mmol) NaOMe, 0.080 g (approx. 0.33 mmol) 5c: yield 0.238 g (80%). Anal. Calcd. for C₃₃H₃₉N₂O₂Pt₂Si₂: C, 54.30; H, 4.56; N, 4.42; S, 6.47%. Found: C, 54.37; H, 4.39; N, 4.29; S, 6.43%. ¹H NMR (CD₂Cl₂, δ, ppm, 500 MHz, 298 K): 7.53–7.47 (m, 12 H, H-Ph), 7.37–7.34 (m, 6 H, H-Ph), 7.23–7.19 (m, 12 H, H-Ph), 3.96–3.92 (m, 2 H, NCH₂), 1.05–1.01 (m, 2 H, CH₂TMS), 0.06 (s, 9 H, CH₂TMS). ¹³C NMR (CD₂Cl₂, δ, ppm, 125 MHz, 298 K): 154.5 (d, ³J_C,P = 13.7 Hz, J_C,P = 3.1 Hz, C-tadtd), 142.1 (dd, ³J_C,P = 15.9 Hz, J_C,P = 3.0 Hz, C-tadtd), 135.4 (dd, ³J_C,P = 10.7 Hz, J_C,P = 6.2 Hz, C-Ph), 131.2 (s, C-Ph), 130.6 (s, C-Ph), 128.1 (dd, ³J_C,P = 10.7 Hz, J_C,P = 5.5 Hz, C-Ph), 44.4 (s, NCH₂), 17.8 (s, CH₂TMS), 1.8 (s, CH₃TMS). ³¹P NMR (CD₂Cl₂, δ, ppm, 202 MHz, 298 K): 17.4 (d, ³J_P,P = 21.0 Hz, P-dppe, Pt-satellites: dd, ¹J_P,P = 2861.0 Hz, ³J_P,P = 20.9 Hz), 16.9 (d, ³J_P,P = 21.0 Hz, P-dppe, Pt-satellites: dd, ¹J_P,P = 2988.1 Hz, ³J_P,P = 20.9 Hz).
31P = 20.9 Hz). 29Si-NMR (CD2Cl2, δ, ppm, 99 MHz, 298 K): 0.6–0.1 (m, Si-TMS). IR (CH2Cl2, ν, cm⁻¹): 3056 (w), 2967 (w), 1437 (m), 1259 (s), 1094 (m), 724 (s), 526 (m).

2.2.5. Synthesis of 10

In a 50 mL Schlenk flask, 5c (0.081 g, approx. 0.35 mmol) were dissolved in THF (50 mL). Next, [(η⁵-C₅H₅)Co(CO)I₂] (0.142 g, 0.35 mmol) and NEt₃ (0.11 mL, 0.76 mmol) were added to the solution. The blue solution was stirred for 4 days at room temperature. The purification was carried out chromatographically with a CH2Cl2/MeOH solvent mixture (20/1) as mobile phase. Crystals suitable for X-ray structural analysis were obtained from a saturated CH2Cl2 solution with n-pentane: yield 0.053 g (43%). 1H NMR (dimer, CDCl3, δ, ppm, 500 MHz, 298 K): 4.80 (s, 5 H, H-C3), 4.42–4.30 (m, 2 H, CH2), 1.49–1.33 (m, 2 H, CH₂TMS), 0.16 (s, 9 H, C11-TMS). 13C NMR (dimer, CDCl3, δ, ppm, 125 MHz, 298 K): 156.0 (C-tazdt), 151.2 (C-tazdt), 88.7 (C-Cp), 45.7 (NCH2), 18.1 (CH3TMS), -1.6 (CH3-TMS). 29Si NMR (dimer, CDCl3, δ, ppm, 99 MHz, 298 K): 1.1–0.4 (m, Si-TMS). MS (ESI-TOF; 9:1 MeOH:H2O with 0.1% HCOOH, m/z): 356 (M + H⁺), 710 (M₂). IR (CH2Cl2, ν, cm⁻¹): 2968 (w), 2879 (w), 1483 (w), 1267 (s), 748 (s), 708 (s), 558 (m).

2.2.6. Synthesis of 11

In a 50 mL Schlenk flask, a solution of 5a (0.103 g, approx. 0.41 mmol) in THF (30 mL) was treated with [(η⁵-C₅H₅)Co(CO)I₂] (0.165 g, 0.41 mmol) and NEt₃ (0.12 mL, 0.90 mmol). The blue solution was stirred for 5 days at room temperature. The purification was carried out chromatographically with a CH2Cl2/MeOH solvent mixture (20/1). Compound 11 was isolated from the first blue fraction. Crystals suitable for X-ray structural analysis were obtained from a saturated CH2Cl2 solution with n-pentane. Yield: 0.008 g (1%).

3. Results and Discussion

3.1. Ligand Synthesis

In contrast to the [3 + 2] cyclization reaction using bis(sulfanyl)acetylene described in a recent publication, mono(sulfanyl)acetylene was used to check whether an insertion of the second benzylsulfanyl group is more advantageous at the cyclized triazole than at the alkyne [16]. The synthesis of the sulfur-substituted triazole derivatives 1a–g was carried out by a CuAAC reaction with an azide bearing the N-protective groups 4-methoxybenzyl (4-MOB), 2-(trimethylsilyl)ethyl (TMS-CH2), 2,6-dimethylphenyl (Xy), benzyl (Bn) or 2-picolyl (2-Pic) and benzylsulfanyl-acetylene (Scheme 1, Table 1). Simply, CuSO4 · 5 H2O was used here as the catalyst system, which was reacted in situ with sodium ascorbate (NaAsc) to obtain the catalytically active Cu(I) (Scheme 1) [5,10,22,23].

After purification by column chromatography, the N-protected 1H-1,2,3-triazole-4-monosulfides were isolated in yields of 36% to 97% (Table 1) and were characterized by NMR spectroscopy. It should be noted that the regioselective cyclization led exclusively to the 4-sulfido derivative, which is in accord with observations of Meldal and Sharpless [5,24]. The introduction of the second sulfur substituent is carried out analogously to the 4-sulfido derivative, which is in accord with observations of Meldal and Sharpless. [25] For this purpose, the corresponding triazoles 1a–g were deprotonated with n-butyllithium at −78 °C, reacted with elemental sulfur and subsequently trapped with benzyl bromide (Scheme 1). After purification by column chromatography, the corresponding triazoles 2a–e were isolated in yields between 38% and 89% (Table 1).

In the 1H NMR spectra, 2 new signals were observed at a chemical shift between 3.55 ppm and 3.79 ppm for the CH2 protons of the introduced benzyl group, while the triazole proton of 1a–g between 7.05 ppm and 7.68 ppm had disappeared (Figures S32–S46). In the case of compound 1g, the introduction of sulfur at 5-position failed.
Due to the electron-withdrawing pyridine substituent in the 2-picoly protective group, the acidity of the methylene proton is higher than that of the triazole proton. Accordingly, deprotonation and subsequent methylation with Mel occurs at the N-2-picoly group to give 3, as can be observed by the doublet $^1\text{H}$ NMR signal at 1.88 ppm for the methyl group attached to the N-protective group (Figure S49). Also in a [3 + 2] cycloaddition of bis(benzylsulfanyl)acetylene and 2-picoly azide with CuSO$_4$/NaAsc as catalyst 2a was not isolated. A terminal acetylene is necessary for an end-on coordination of the Cu$^i$ to catalyze the [3 + 2] cycloaddition [10].
Nevertheless, this new two-step method for the generation of a disulfide unit on the 1H-1,2,3-triazole shows clear advantages in comparison with the synthesis described in the literature. Thus, sensitive and expensive catalyst systems [(NHC)CuI] and [(η⁵-C₅Me₅)(cod)RuCl] are dispensable [16]. Moreover, anaerobic and anhydrous conditions are not necessary in the first reaction steps and the overall yields are higher. While Schallenberg et al. achieved a yield of 39% with the benzyl group, a yield of 65% was realized with the new route [16]. Accordingly, it was also investigated whether the disulfide unit can be introduced stepwise into a 1,2,3-triazole by the direct method. For this purpose, the unsubstituted 1-(4-methoxybenzyl)-1H-1,2,3-triazole was deprotonated with n-butyllithium and subsequently reacted with elemental sulfur and benzyl bromide for alkylation (Scheme 1). After chromatographic purification, the 1H NMR spectrum of the isolated product 4 revealed a methylene singlet at 3.67 ppm and a triazole proton at 7.48 ppm, indicating introduction of the sulfur in 5- instead of 4-position (Figure S52). Interestingly, a preference for the 5-substituted derivatives was also observed by Fokin et al. by ruthenium-catalyzed [3 + 2] cycloadditions of terminal alkynes with azides [26–28]. The regioselective deprotonation can be explained by the greater stabilization of the carbanion in 5-position due to resonance (Figure 1). Consistently, a subsequent introduction of the second sulfur substituent at 4-position by the same procedure proved unsuccessful. Respective attempts always led to the recovery of the starting material, which can be attributed to a lack of resonance stabilization in the carbanion.

![Figure 1. Mesomeric structures after deprotonation.](image)

To enable coordination via dithiolene unit, the benzyl protective groups on sulfur must be removed. Due to having the best yields, compounds 2a–c were used for coordination experiments. As we previously reported, this could readily be achieved by reductive removal with elemental sodium in presence of naphthalene in THF [16]. After an acidic work-up, the corresponding dithiols 5a–c were isolated as yellow oils in reasonable yields (Scheme 1). The samples are not analytically but sufficiently pure for coordination experiments (vide infra).

### 3.2. Synthesis of Metal Complexes

Coordination experiments with 1H-1,2,3-triazoles-4,5-dithiols were performed with particular attention to the regioselective dithiolate over N-coordination. The dithiols H₂-5a–c were reacted with the first-row and group-10 transition metals CoIII, NiII, PdII and PtII. The CoIII complex 10 was synthesized by reacting the ligand H₂-5c with [{η⁵-C₅H₅}Co(CO)I₂] in THF in presence of NEt₃ (Scheme 2). The reaction progress could be observed by a decrease of the CO band in IR spectroscopy and the reaction solution turning blue.

In contrast to the free dithiol H₂-5c, the corresponding complex could be purified by flash chromatography, such that a dark purple compound was isolated and identified as the Co-complex 10. Further, the dppe-complexes 6 and 7 with group-10 metals were obtained either by reaction of H₂-5b in a two-phase system (CH₂Cl₂/H₂O) with KOH and the precursors [{dppe}MCl₂] [M = Ni, Pd; dppe = 1,2-bis(diphenylphosphino)ethane] or with [{dppe}PtCl₂] and [{PPh₃}₂PtCl₂], respectively, in MeOH using NaOMe as a base. After aqueous work-up and chromatographic purification, a green Ni compound (6), a reddish Pd compound (7) and yellow Pt compounds (8 and 9a–c) were isolated.

In addition to the main products, by-products were surprisingly isolated from the reaction mixtures with the crude dithiol H₂-5a and corresponding metal precursors (Scheme 3). From the reaction with [{η⁵-C₅H₅}Co(CO)I₂], a tetranuclear complex 11 and from the reaction with [{PPh₃}₂PtCl₂] the by-product 12 were isolated and crystallized.
which are by-products, all complexes exhibited an exclusive dithiolato coordination. The XRD analysis (Figures 2, 3, S4 and S5). With the exception of the complexes from the reaction with [(PPh₃)₂PtCl₂] the by-product 12 were isolated and crystallized. In contrast to the free dithiol H₂- the Co-complex (11) and yellow Pt compounds (12). In addition to the main products, by-products were surprisingly isolated from the reaction mixtures with the crude dithiol H₂-. The molecular structures of all complexes – 6–12 were determined by single-crystal XRD analysis (Figures 2, 3, S4 and S5). With the exception of the complexes 11 and 12, which are by-products, all complexes exhibited an exclusive dithiolato coordination. The molecular structures of the group-10 metals showed the expected square planar geometry, including a planar dithiolate unit. The deviation from the SCCS planarity fell between 1.0(5)° and 3.1(3)°, which is very much in accordance with the values described in the literature [29]. Table 2 lists selected bond lengths and angles. In comparison to classical dithiolene complexes, a larger obtuse bite angle and, related to that, somewhat longer metal–sulfur bonds are evident [30–33]. The former follows the geometric requirements of a five-membered backbone ring, in which a regular internal angle leads to a formal C–C–S angle of 126°. In addition, comparison of the metric parameters in compounds 9a and 9b does not show any influence by the protective group on nitrogen in the bonding situation at the dithiolate unit.

Scheme 2. Coordination of 5²⁻ at Ni²⁺ (6), Pd²⁺ (7), Pt²⁺ (8) and Co³⁺ (10) (base = KOH or NaOMe).

Scheme 3. Coordination to by-products 11 and 12.

3.3. Molecular Structure of the Complexes

The molecular structures of all complexes 6–12 were determined by single-crystal XRD analysis (Figures 2, 3, S4 and S5). With the exception of the complexes 11 and 12, which are by-products, all complexes exhibited an exclusive dithiolato coordination. The molecular structures of the group-10 metals showed the expected square planar geometry, including a planar dithiolate unit. The deviation from the SCCS planarity fell between 1.0(5)° and 3.1(3)°, which is very much in accordance with the values described in the literature [29]. Table 2 lists selected bond lengths and angles. In comparison to classical dithiolene complexes, a larger obtuse bite angle and, related to that, somewhat longer metal–sulfur bonds are evident [30–33]. The former follows the geometric requirements of a five-membered backbone ring, in which a regular internal angle leads to a formal C–C–S angle of 126°. In addition, comparison of the metric parameters in compounds 9a and 9b does not show any influence by the protective group on nitrogen in the bonding situation at the dithiolate unit.
Figure 2. Molecular structure of 6–8, 11 and 12 in the crystal with ellipsoids set at 50% probability. Hydrogen atoms have been omitted for clarity and phenyl or 4-methoxybenzyl (11) substituents are displayed as wireframe.

Figure 3. Molecular structure of the dimer 10 in the crystal with ellipsoids set at 50% probability. Hydrogen atoms have been omitted for clarity and \( \eta^5 \)-C\(_5\)H\(_5\) rings are displayed as wireframe.
Table 2. Comparison of essential bond lengths [Å] and bite angles [°].

<table>
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<tr>
<th></th>
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<td>2.199(1)</td>
<td>2.187(1)</td>
<td>95.80(4)</td>
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<td>1.719(3)</td>
<td>1.750(3)</td>
<td>1.370(4)</td>
<td>2.1982(8)</td>
<td>2.1925(8)</td>
<td>96.09(3)</td>
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<td>7</td>
<td>1.725(5)</td>
<td>1.746(8)</td>
<td>1.381(5)</td>
<td>2.354(2)</td>
<td>2.334(1)</td>
<td>92.99(5)</td>
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<td>1.7400(17)</td>
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<td>[dppe]Pt(dmit)] [34]</td>
<td>1.710(11)</td>
<td>1.716(11)</td>
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<tr>
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<td>1.750(3)</td>
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<td>2.353(6)</td>
<td>91.08(4)</td>
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<td>1.750(3)</td>
<td>1.349(6)</td>
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<td>2.3192(11)</td>
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<td>1.734(11)</td>
<td>1.765(11)</td>
<td>1.384(18)</td>
<td>2.211(2)</td>
<td>2.214(3)/2.270(3)</td>
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<td>1.783(3)</td>
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<td>2.230(1)/2.272(1)</td>
<td>89.73(4)</td>
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<td>11</td>
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<td>1.739(2)</td>
<td>1.379(2)/1.379(3)</td>
<td>2.2601(7)</td>
<td>2.2721(6)</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>1.747(3)</td>
<td>1.379(4)</td>
<td>2.3274(7)</td>
<td>2.3274(7)</td>
<td>-</td>
<td>-</td>
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</tbody>
</table>

dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate; dmit = 1,3-dithiole-2-thione-4,5-dithiolate.

Moreover, when replacing the metal center from NiII (6) to PdII (7) or PtII (8), the dithiolate moiety does not show significant differences in the bond lengths C1–C2 with 1.368(6) Å to 1.381(5) Å or C1–S1 and C2–S2, which are between 1.725(5) Å and 1.748(6) Å. On the other hand, the M–S bond lengths show a distinct elongation by going from NiII to PdII and PtII, which is essentially related to the increasing size of the metal atom. However, the bond lengths Pd–S in 7 {2.354(2) Å and 2.334(1) Å} and Pt–S in 8 {2.349(1) Å and 2.335(1) Å} are virtually equal. This effect is well-known and is attributed to the relativistic effect of the Pt atom and the resulting shrinking of the d orbitals [34].

The molecular structure of 10 in the solid state reveals a dimerization, in which not only is the CoIII center coordinated by one dithiolate unit, but a third sulfur atom of a neighboring dithiolate moiety is bound to cobalt and vice versa. The observed dimerization to (10)2 can be rationalized by fulfilling the 18 valence electron rule. On the other hand, the monomer constitutes a 16 valence electron complex, which is less stable but more readily solvated due to the free coordination site. Such dimerization equilibria are regularly observed in related [(η5-C5H5Co(dithiolene)] complexes [32,33,37–40].

If the η5-C5H5 ring is considered as occupying a single coordination site, the CoIII centers show a τ-parameter of 0.76, which is close to τ = 1 of a tetrahedron [41]. The bond length M–S2* of 2.269(1) Å is comparable to that of M–S1 {2.278(2) Å} and M–S2 {2.271(1) Å}. In studies on the compounds [CpCo(Cl3bdt)]2 and [CpCo(bdt)]2 (bdt = benzene-1,2-dithiolate), the Co-S bond lengths fall between 2.211(2) Å and 2.246(1) Å and are again slightly shorter than the bond lengths determined in 10. [32,33] Accordingly, as described in the literature, the distance between the Co centers between 3.212(6) Å and 3.2893(4) Å is slightly larger than the distance determined in 10 with 3.3055(9) Å. None correspond to a direct Co-Co bond of 2.32 Å. [21].

A by-product of the reaction of H2–5a with [η5-C5H5Co(CO)]2 was isolated after chromatography and crystallization. The crystal structure of 11 undisclosed an unexpected tetranuclear complex, in which the CoIII ions are linked in a cyclic fashion by N-4-methoxybenzyl-1,2,3-triazole-5-thiolate ligands (Figure 2). Herein, each CoIII is coordinated by a thiolate of one triazole and by a nitrogen atom in the third position of another. The coordination sphere of each CoIII center is saturated by one iodide and one η5-C5H5 ligand. This structural motif uncovered the loss of one thiolate substituent at 4-position of the 1,2,3-triazole ligand.
Likewise, the triazole ligands in the by-product 12 do not contain a dithiolate unit. Instead, the two triazole ligands in 12, next to two trans-standing triphenylphosphine ligands, are coordinated via one remaining thiolate in 4-position in a quadratic planar geometry around a Pt\textsuperscript{II} center. A comparison of complex 12 with 9a with respect to the influence of cis/trans configuration is interesting, because the ligands are highly similar. The trans arrangement leads to longer Pt–P1/P1* bonds (2.3220(8) Å) in 12 compared to the cis arrangement in 9a with Pt–P1/P2: 2.2853(7) Å/2.2944(7) Å, which reflects some symbiotic $\pi$-bonding effect in 9a. The successful isolation of low-yield by-products 11 and 12 indicate limitation of side reactions in the reductive removal of the thiol protective groups. Remarkably, the cleavage of the whole benzylthiolate is possible both at 4- and 5-position.

3.4. NMR Spectroscopy of Metal Complexes

The phosphine ligands in the complexes 6–8 and 9a–c are valuable probes for the electronic situation of the metal, which can be investigated by $^{31}$P NMR spectroscopy. The Ni complex 6 as well as the Pd compound 7 show two doublets at chemical shifts of 58.7/60.5 ppm, and 56.1/58.4 ppm, respectively. The observed doublets result from the C\textsubscript{1} symmetry and the related chemical non-equivalence of the phosphorus atoms. Consistently, a slightly smaller coordination chemical shift $\Delta\delta$ of the Pd-dppe signals is combined with a lower $^{31}$P/$^{31}$P coupling constant of 18.0 Hz. The Ni-dppe complex 6 shows a substantially larger coupling constant of 47.9 Hz. The doublet signals for the corresponding Pt\textsuperscript{II} compound 8 were detected at 45.4 ppm and 45.7 ppm, with a coupling constant of 10.5 Hz confirming the trend $J_{PP}(\text{Ni}) > J_{PP}(\text{Pd}) > J_{PP}(\text{Pt})$ and $\delta(\text{Ni}) > \delta(\text{Pd}) > \delta(\text{Pt})$. Related observations were already reported for [(dppe)M(mnt)] ($\text{mnt} = \text{maleonitriledithiolate}$) serving as a selected example [29].

With the change of the ligand dppe to PPh\textsubscript{3} in compounds 9a–c, two doublets are observed at the chemical shift between 16.7 ppm and 17.7 ppm. In addition to the $^{31}$P/$^{195}$Pt coupling constants ($J_{PP} = 21.0$ Hz), $^{31}$P/$^{195}$Pt coupling constants between 2861 Hz and 2998 Hz are observed (Table 3), which are in good agreement with other dithiolene-Pt compounds [31,42,43].

<table>
<thead>
<tr>
<th>M</th>
<th>$\delta$ [ppm]</th>
<th>$J_{PP}$ [Hz]</th>
<th>$J_{PP}$ [Hz]</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Ni 60.5/58.7</td>
<td>47.9</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>Pd 58.4/56.1</td>
<td>18.0</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>Pt 45.7/45.4</td>
<td>10.5</td>
<td>2778/2760</td>
</tr>
<tr>
<td>9a</td>
<td>Pt 17.2/17.1</td>
<td>21.0</td>
<td>2915/2943</td>
</tr>
<tr>
<td>9b</td>
<td>Pt 17.7/16.7</td>
<td>20.0</td>
<td>2862/2998</td>
</tr>
<tr>
<td>9c</td>
<td>Pt 17.4/16.9</td>
<td>20.0</td>
<td>2861/2988</td>
</tr>
</tbody>
</table>

Here, the PPh\textsubscript{3} is particularly well-suited for observing changes in the electronic situation of the complex by means of $^{31}$P-NMR spectroscopy [42]. The individual N-protective group in 9a–c exerts only a minor influence on the $^{31}$P/$^{195}$Pt coupling constant. However, the slightly differing trans effect of the asymmetric dithiolate on the phosphines is reflected in the variance of the $^{31}$P/$^{195}$Pt coupling constant, spanning $\Delta J$ range from 28 Hz (9a) to 136 Hz (9b).

3.5. Electronic Structure Elucidation

The different electronic situation in compounds 6–8 is revealed by UV/Vis spectroscopy and cyclic voltammetry. Figure 4 shows the UV/Vis spectra of compounds 6, 7 and 8. In the visible range between 400 and 700 nm characteristic absorption bands at 409 nm (8), 523 nm (7) and 602 nm (6) are observed, which are responsible for the characteristic color of the compounds: green (6), red (7) and yellow (8). According to TD-DFT calculations, the underlying excitation can be assigned to a dithiolate-$\pi$ to metal-d transition. Hence, the trend 6 $>$ 7 $>$ 8 in $\lambda$ reflect the increasing ligand field splitting in the
order Ni, Pd, Pt. Consistently, in cyclic voltammetry, a reduction process requires lower potentials for heavier metals. The Ni compound 6 shows a reversible NiII/NiI reduction with a half-step potential of −1.79 V, while an irreversible signal at a potentials of −2.14 V and −2.60 V, respectively, are observed for complexes 7 and 8. DFT calculations on related Ni and Pd dppe complexes of N-2,6-dimethylphenyltriazole-4,5-dithiolate and the corresponding anions resulted that the reversible reduction NiII,1 is based on a substantial distortion to tetrahedral, which is not relevant for Pd and Pt. Accordingly, the calculated ΔG value for the reduction are higher for Pd and Pt compared with Ni. [16].

The dimerization of complex 10 to form (10)_2 found in the solid state could be of great interest for the assembly of coordination polymers on multiple N-coordinated triazole ligands at one metal ion. Therefore, the dimerization equilibrium in solution was investigated by 1H NMR and UV/Vis spectrometry as well as cyclic voltammetry. Variable temperature 1H NMR demonstrated that at concentrations of about 0.02 mol/L, the dimer at 4.79 ppm prevails (Figure 5, right), while the monomer is detected at 5.48 ppm. A dimerization constant K_D of 290 L/mol was determined at 25 °C and a Van’t-Hoff plot of K_D at decreasing temperatures resulted a ΔH value of −10.63 kcal/mol and ΔS of −23.6 cal/mol-K (Figure S89). In contrast, in UV/Vis spectroscopy at about 2 × 10⁻⁴ mol/L in CH₂Cl₂ the monomer is dominant. The violet crystals yielded a dark blue solution. Two absorption bands, at 485 nm and 619 nm, respectively, were observed in the visible range. For the solid state, reflectance UV/Vis spectroscopy was carried out (Figure 5, left). The absorption bands at 351 nm and 510 nm apparently belong to the dimer (10)_2. Accordingly, the strongest absorption band at 619 nm is assigned to a dithiolate-π to CoIII charge transfer in the monomer 10. Compared to the complex [(η⁵-C₅H₅)Co(bdt)] (λ = 566 nm), the band is bathochromically shifted by 1500 cm⁻¹. [44] This difference can be attributed to the stronger dithiolate character in 1H-1,2,3-triazole-4,5-dithiolate ligands compared with the benzene-1,2-dithiolate, which shows a stronger conjugation to the aromatic system due to better electronegativity matching. Comparable charge transfer bands were reported for many other semi-sandwich complexes with a cobalt dithiolene ligand. [45–47] As expected, the equilibrium between the monomer and the dimer can be influenced by changing the temperature between 0 °C and 40 °C. An increased temperature results in an increased concentration of the monomer at 619 nm.

The cyclic voltammograms of 10 were measured at a concentration range, at which the dimer (10)_2 is the main species (Figure 6). The signal at a potential E_1/2 of −0.99 V for the CoIII/CoII redox couple exhibits quasi-reversible features. The peak difference increases from 370 mV at a scan rate of 100 mV/s to 520 mV at 300 mV/s, which supports a weakly coupled two-electron process for (10)_2. In addition, irreversible oxidation at about +0.8 V causes the appearance of a new signal at slightly higher potential compared with the
original CoII/CoIII couple. This can reasonably be assigned to the monomer, because, being easier to reduce, the 16 valence electron monomer 10 should exhibit a higher potential. Apparently, one-electron oxidation leads to a release of the monomer 10.

Figure 5. Temperature dependent spectra of 10/(10)2: UV/Vis spectra in CH2Cl2 solution and solid state (left) and 1H NMR spectra in CD2Cl2 (*) (right).

Figure 6. Cyclic voltammograms of the compound 10 in CH2Cl2 at different scan rates (left) and changes in the course of multiple potential scans (right).

4. Conclusions

In this publication, a new synthetic route for the assembly of 1H-1,2,3-triazole-4,5-dithiolenes was presented, which made use of click chemistry. Instead of complicated, expensive and sensitive catalysts, very high yields of the mono-substituted triazole sulfides 1 could be achieved using CuSO4 in CuAAC. The second sulfur substituent could be introduced by facile deprotonation of the triazole ring and subsequent reaction with sulfur and benzyl bromide, yielding the triazole disulfides 2. Nevertheless, this new synthetic method for the generation of a dithiolene unit at the 1H-1,2,3-triazole shows clear advantages in comparison with the synthesis described in the literature. [16] In addition, all attempts at a direct introduction of both sulfide substituents into the prototype 1H-1,2,3-triazole led exclusively to the monosulfide isomers 4. Subsequent reductive removal of the S-protective groups with sodium in THF in the presence of naphthalene yielded the desired dithiol derivatives. However, by-products indicating a competing removal of the whole benzyl thiolate at either 4-or 5-position, respectively, were isolated in form of CoIII and PtII complexes (11 and 12). In coordination experiments with the dithiols, several complexes with NiII, PdII, PtII and CoIII could be isolated and fully characterized. It was shown that dithiolate coordination dominates the coordination behavior. Neither the coordinated metal (6, 7, 8) nor the protective group at the nitrogen atom of the triazole (9a-c) have a strong effect on the electronic situation at the dithiolate unit. With coordination of the [η5-C3H5]Co moiety, a 16 valence electron CoIII center could be introduced at the
dithiolate unit giving complex 10. Instead of a conceivable coordination of a triazole N atom, this complex showed a dimerization via dual μ-sulfur coordination in the solid state. By means of a temperature-dependent NMR and UV/Vis spectroscopic measurements completed by cyclic voltammetry, the thermodynamic parameters of the monomer–dimer equilibrium were determined.

**Supplementary Materials:** The following supporting information can be downloaded at: [https://www.mdpi.com/article/10.3390/chemistry5020086/s1, Tables S1–S4: Crystallographic details for 1d, 1g, 2a, 6–9b and 10–12; Figure S1: Molecular structure of 1d in the crystal; Figure S2: Molecular structure of 2a in the crystal; Figure S4: Molecular structure of 9a in the crystal; Figure S5: Molecular structure of 9b in the crystal; Materials, Measurements and Synthese of organic products (1–4); Figure S6: 1H NMR spectrum (300 MHz) of 2,4-dimethoxybenzyl azide in CDCl$_3$ at 298 K; Figure S7: IR spectroscopy of 2,4-dimethoxybenzyl azide in THF; Figure S8: 1H NMR spectrum (300 MHz) of 2-(trimethylsilyl)ethyl azide with traces of n-hexane in CDCl$_3$ at 298 K; Figure S9: 13C NMR spectrum (75 MHz) of 2-(trimethylsilyl)ethyl azide with traces of n-hexane in CDCl$_3$ at 298 K; Figure S10: 29Si NMR spectrum (60 MHz) of 2-(trimethylsilyl)ethyl azide in CDCl$_3$ at 298 K; Figure S11: IR spectroscopy of 2-(trimethylsilyl)ethyl azide in Et$_2$O with traces of DMF; Figure S12: 1H NMR spectrum (500 MHz) of 1a in CDCl$_3$ at 298 K; Figure S13: 13C NMR spectrum (125 MHz) of 1a in CDCl$_3$ at 298 K; Figure S14: IR spectroscopy of 1a in CH$_2$Cl$_2$; Figure S15: 1H NMR spectrum (300 MHz) of 1b in acetone-D$_6$ at 298 K; Figure S16: 13C NMR spectrum (75 MHz) of 1b in CDCl$_3$ at 298 K; Figure S17: IR spectroscopy of 1b in CH$_2$Cl$_2$; Figure S18: 1H NMR spectrum (300 MHz) of 1c in CDCl$_3$ at 298 K; Figure S19: 13C NMR spectrum (75 MHz) of 1c in CDCl$_3$ at 298 K; Figure S20: 29Si NMR spectrum (60 MHz) of 1c in CDCl$_3$ at 298 K; Figure S21: 1H NMR spectrum (300 MHz) of 1d in CDCl$_3$ at 298 K; Figure S22: 13C NMR spectrum (75 MHz) of 1d in CDCl$_3$ at 298 K; Figure S23: IR spectroscopy of 1d in CH$_2$Cl$_2$; Figure S24: 1H NMR spectrum (500 MHz) of 1e in CDCl$_3$ at 298 K; Figure S25: 13C NMR spectrum (75 MHz) of 1e in CDCl$_3$ at 298 K; Figure S26: IR spectroscopy of 1e in CH$_2$Cl$_2$; Figure S27: 1H NMR spectrum (300 MHz) of 1f in acetone-D$_6$ at 298 K; Figure S28: 13C NMR spectrum (75 MHz) of 1f in acetone-D$_6$ at 298 K; Figure S29: IR spectroscopy of 1f in CH$_2$Cl$_2$; Figure S30: 1H NMR spectrum (300 MHz) of 1g in CDCl$_3$ at 298 K; Figure S31: 13C NMR spectrum (75 MHz) of 1g in CDCl$_3$ at 298 K; Figure S32: 1H NMR spectrum (250 MHz) of 2a with traces of EtOAc in CDCl$_3$ at 298 K; Figure S33: 13C NMR spectrum (75 MHz) of 2a in CDCl$_3$ at 298 K; Figure S34: IR spectroscopy of 2a in CH$_2$Cl$_2$; Figure S35: 1H NMR spectrum (300 MHz) of 2b in CDCl$_3$ at 298 K; Figure S36: 13C NMR spectrum (75 MHz) of 2b in CDCl$_3$ at 298 K; Figure S37: IR spectroscopy of 2b in CH$_2$Cl$_2$; Figure S38: 1H NMR spectrum (300 MHz) of 2c in CDCl$_3$ at 298 K; Figure S39: 13C NMR spectrum (75 MHz) of 2c in CDCl$_3$ at 298 K; Figure S40: 29Si NMR spectrum (60 MHz) of 2c in CDCl$_3$ at 298 K; Figure S41: IR spectroscopy of 2c in CH$_2$Cl$_2$; Figure S42: 1H NMR spectrum (300 MHz) of 2d in CDCl$_3$ at 298 K; Figure S43: IR spectroscopy of 2d in CH$_2$Cl$_2$; Figure S44: 1H NMR spectrum (500 MHz) of 2e in CD$_2$Cl$_2$ at 298 K; Figure S45: IR spectroscopy of 2e in CH$_2$Cl$_2$; Figure S46: 1H NMR spectrum (500 MHz) of 2f in CDCl$_3$ at 298 K; Figure S47: 13C NMR spectrum (126 MHz) of 2f in CDCl$_3$ at 298 K; Figure S48: IR spectroscopy of 2f in CH$_2$Cl$_2$; Figure S49: 1H NMR spectrum (300 MHz) of 3 in CDCl$_3$ at 298 K; Figure S50: 13C NMR spectrum (75 MHz) of 3 in CDCl$_3$ at 298 K; Figure S51: IR spectroscopy of 3 in CH$_2$Cl$_2$; Figure S52: 1H NMR spectrum (300 MHz) of 4 in CDCl$_3$ at 298 K; Figure S53: 13C NMR spectrum (75 MHz) of 4 in CDCl$_3$ at 298 K; Figure S54: IR spectroscopy of 4 in CH$_2$Cl$_2$; Figure S55: 1H NMR spectrum (300 MHz) of 5a in CDCl$_3$ at 298 K; Figure S56: IR spectroscopy of 5a in CH$_2$Cl$_2$; Figure S57: 1H NMR spectrum (300 MHz) of 5b in CD$_2$Cl$_2$ at 298 K; Figure S58: IR spectroscopy of 5b in CH$_2$Cl$_2$; Figure S59: 1H NMR spectrum (300 MHz) of 5c in THF-D$_8$ at 298 K; Figure S60: 1H NMR spectrum (300 MHz) of 6 with traces of CH$_3$Cl in CDCl$_3$ at 298 K; Figure S61: 13C NMR spectrum (75 MHz) of 6 in CDCl$_3$ at 298 K; Figure S62: 31P NMR spectrum (122 MHz) of 6 in CDCl$_3$ at 298 K; Figure S63: IR spectroscopy of 6 in CH$_2$Cl$_2$; Figure S64: 1H NMR spectrum (300 MHz) of 7 with traces of CH$_3$Cl$_2$ and CH$_2$OH in DMF-D$_7$ at 298 K; Figure S65: 13C NMR spectrum (75 MHz) of 7 in DMF-D$_7$ at 298 K; Figure S66: 1H NMR spectrum (122 MHz) of 7 in DMF-D$_7$ at 298 K; Figure S67: IR spectroscopy of 7 in CH$_2$Cl$_2$; Figure S68: 2H NMR spectrum (300 MHz) of 8 in CD$_2$Cl$_2$ at 298 K; Figure S69: 13C NMR spectrum (75 MHz) of 8 in CD$_2$Cl$_2$ at 298 K; Figure S70: 31P NMR spectrum (122 MHz) of 8 in CD$_2$Cl$_2$ at 298 K; Figure S71: IR spectroscopy of 8 in CH$_2$Cl$_2$; Figure S72: 1H NMR spectrum (500 MHz) of 9a with traces of CH$_3$Cl$_2$ in CD$_2$Cl$_2$ at 298 K; Figure S73: 13C NMR spectrum (125 MHz) of 9a in CD$_2$Cl$_2$ at 298 K; Figure S74: 31P NMR spectrum (202 MHz) of 9a in CD$_2$Cl$_2$ at 298 K; Figure S75: IR spectroscopy of 9a in CH$_2$Cl$_2$; Figure S76: 1H NMR spectrum (500 MHz) of 9b with traces of CH$_2$Cl$_2$ in CD$_2$Cl$_2$ at 298 K; Figure S77: 13C NMR spectrum
(125 MHz) of \(9b\) in CD\(_2\)Cl\(_2\) at 298 K; Figure S78: \(^{31}\)P NMR spectrum (202 MHz) of \(9b\) in CD\(_2\)Cl\(_2\) at 298 K; Figure S79: IR spectroscopy of \(9b\) in CH\(_2\)Cl\(_2\); Figure S80: \(^1\)H NMR spectrum (500 MHz) of \(9c\) with traces of CH\(_2\)Cl\(_2\) in CD\(_2\)Cl\(_2\) at 298 K; Figure S81: \(^{13}\)C NMR spectrum (125 MHz) of \(9c\) in CD\(_2\)Cl\(_2\) at 298 K; Figure S82: \(^{29}\)Si NMR spectrum (99 MHz) of \(9c\) in CD\(_2\)Cl\(_2\) at 298 K; Figure S83: \(^{31}\)P NMR spectrum (202 MHz) of \(9c\) in CD\(_2\)Cl\(_2\) at 298 K; Figure S84: IR spectroscopy of \(9c\) in CH\(_2\)Cl\(_2\); Figure S85: \(^1\)H NMR spectrum (500 MHz) of 10 in CDCl\(_3\) at 298 K; Figure S86: \(^{13}\)C NMR spectrum (125 MHz) of 10 in CDCl\(_3\) at 298 K; Figure S87: \(^{29}\)Si NMR spectrum (99 MHz) of 10 in CDCl\(_3\) at 298 K; Figure S88: IR spectroscopy of 10 in CH\(_2\)Cl\(_2\); Figure S89: Van’t Hoff-plot of the monomer-dimer equilibrium 10/(10)_2.

References [25,48–63] are cited in Supplementary Materials.

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References

3. Lewis, W.G.; Green, L.G.; Grynszpan, F.; Radič, Z.; Carlier, P.R.; Taylor, P.; Finn, M.G.; Sharpless, K.B. Click Chemistry In Situ: Acetylcholinesterase as a Reaction Vessel for the Selective Assembly of a Femtomolar Inhibitor from an Array of Building Blocks. Angew. Chem. Int. Ed. 2002, 41, 1053–1057. [CrossRef]
6. Clarke, D.; Mares, R.W.; McNab, H. Preparation and pyrolysis of 1-(pyrazol-5-yl)-1,2,3-triazoles and related compounds. Chem. Soc. Rev. 2010, 39, 70–83. [CrossRef]
10. Hein, J.E.; Fokin, V.V. Copper-catalyzed azide-alkyne cycloaddition (CuAAC) and beyond: New reactivity of copper(I) acetylides. Chem. Soc. Rev. 2010, 39, 1302–1315. [CrossRef]
13. Crowley, J.D.; Bandeen, P.H.; Hanton, L.R. A one pot multi-component CuAAC “click” approach to bidentate and tridentate pyridyl-1,2,3-triazole ligands: Synthesis, X-ray structures and copper(II) and silver(I) complexes. Polyhedron 2010, 29, 70–83. [CrossRef]


