

Acetylenedithiolate – Alkyne Complex Formation Renders it a Dithiolate Chelate Ligand

Wolfram W. Seidel,* Markus Schaffrath and Tania Pape

Supplemental material

1. Experimental and spectroscopic data of the bis(metalla-acetylenedithiolate)complexes 2-4.

[{Tp'W(CO)₂(μ-η²-C,C'-η²-S,S'-(C₂S₂)}₂Ni] **2**. A solution of 80 mg (0.167 mmol) [Ni(CH₃CN)₆](BF₄)₂ in 20 ml CH₂Cl₂ was added to a stirred solution of 222 mg (0.334 mmol) K-1 in 15 ml THF. The colour of the solution turned blue immediately. After 5 hours the solvents were removed in *vacuo*. The residue was dissolved in a minimum amount of THF and transferred on a chromatography column containing SiO₂ and toluene. The product **2** was eluted with a toluene/THF mixture (v/v: 5/1). The eluate was reduced in volume to 5 ml yielding 24 mg of **2** (11 %) as a blue powder. Single crystals of **2** suitable for X-ray structure analysis are obtained from the eluate without any solvent reduction in the course of two weeks.

Anal. Calcd. for **2**·2 toluene, C₅₂H₆₀B₂N₁₂O₄S₄NiW₂: C, 41.82; H, 4.05; N, 11.25. Found: C, 41.68; H, 3.98; N, 11.14.

IR (KBr) $\tilde{\nu}$ = 2556 (m, BH), 2008 (s, CO), 1957 cm⁻¹ (s, CO).

¹H NMR (CD₂Cl₂, 400 MHz, 298 K): δ = 5.93 (s, 1 H, CH(CCH₃)₂), 5.92 (s, 2 H, CH(CCH₃)₂), 2.49 (s, 3 H, CCH₃), 2.40 (s, 6 H; CCH₃), 2.34 (s, 3 H, CCH₃), 2.31 ppm (s, 6 H, CCH₃).

¹³C NMR (CD₂Cl₂, 100.6 MHz, 298 K): δ = 216.3 (WCO), 154.1, 153.7, 147.2, 145.2 (CH(CCH₃)₂), 108.2, 107.5 (CH(CCH₃)₂), 15.7, 15.2, 12.6, 12.3 ppm (CCH₃), the alkyne resonances are in coalescence.

UV/Vis (CH₂Cl₂): λ_{\max} (ϵ) = 315 (29500), 374 (42000), 649 nm (19000 M⁻¹cm⁻¹).

[{Tp'W(CO)₂(μ-η²-C,C'-η²-S,S'-(C₂S₂)}₂Pd] **3**. A solution of 70 mg (0.158 mmol) [Pd(CH₃CN)₄](BF₄)₂ in 10 ml CH₃CN was added to a stirred solution of 210 mg (0.316 mmol) K-1 in 15 ml THF. The colour of the solution turned intensely red immediately. After 5 hours the solvents were removed in *vacuo*. The residue was dissolved in a minimum amount

of THF and transferred on a chromatography column containing SiO₂ and toluene. The product **3** was eluted with toluene. The eluate was reduced in volume to 5 ml yielding 22 mg of **3** (10 %) as red powder. Single crystals of **3** suitable for X-ray structure analysis are obtained from the eluate without any volume reduction in the course of two weeks.

Anal. Calcd. for **3**·2 toluene, C₅₂H₆₀B₂N₁₂O₄S₄PdW₂: C, 40.53; H, 3.92; N, 10.91. Found: C, 40.61; H, 3.95; N, 10.84.

IR (KBr) $\tilde{\nu}$ = 2555 (m, BH), 2010 (s, CO), 1959 cm⁻¹ (s, CO).

¹H NMR (CD₂Cl₂, 400 MHz, 298 K): δ = 5.94 (s, 2 H, CH(CCH₃)₂), 5.93 (s, 1 H, CH(CCH₃)₂), 2.50 (s, 3 H, CCH₃), 2.40 (s, 6 H; CCH₃), 2.34 (s, 3 H, CCH₃), 2.33 ppm (s, 6 H, CCH₃).

¹³C NMR (CD₂Cl₂, 100.6 MHz, 298 K): δ = 216.2 (WCO), 154.2, 153.7, 147.3, 145.3 (CH(CCH₃)₂), 108.3, 107.5 (CH(CCH₃)₂), 15.7, 15.2, 12.6, 12.3 (CCH₃), the alkyne resonances are in coalescence.

UV/Vis (CH₂Cl₂): λ_{\max} (ϵ) = 341 (38500), 501 nm (41000 M⁻¹cm⁻¹).

[{Tp'W(CO)₂(μ - η^2 -C,C'- η^2 -S,S'-(C₂S₂)}₂Pt] **4.** A solution of 30 mg (0.0636 mmol) [Pt(PhCN)₂Cl₂] in 7 ml CH₂Cl₂ was added to a stirred solution of 84 mg (0.127 mmol) K-**1** in 7 ml THF. The colour of the solution turned intensely blue in the course of 16 hours. The solvents were removed in *vacuo*. The residue was dissolved in a minimum amount of THF and transferred on a chromatography column containing SiO₂ and toluene. The product **4** was eluted with toluene. The eluate was reduced in volume to 5 ml yielding 17 mg of **4** (19 %) as a blue powder. Single crystals of **4** suitable for X-ray structure analysis are obtained from the eluate without any volume reduction in the course of two weeks.

Anal. Calcd. for **4**·2 toluene, C₅₂H₆₀B₂N₁₂O₄S₄PtW₂: C, 38.32; H, 3.71; N, 10.31. Found: C, 38.33; H, 3.75; N, 10.21.

IR (KBr) $\tilde{\nu}$ = 2556 (m, BH), 2009 (s, CO), 1956 cm⁻¹ (s, CO).

¹H NMR (CD₂Cl₂, 400 MHz, 298 K): δ = 5.94 (s, 1 H, CH(CCH₃)₂), 5.92 (s, 2 H, CH(CCH₃)₂), 2.52 (s, 3 H, CCH₃), 2.40 (s, 6 H, CCH₃), 2.34 (s, 3 H, CCH₃), 2.21 ppm (s, 6 H, CCH₃).

¹³C NMR (CD₂Cl₂, 100.6 MHz, 298 K): δ = 215.7 (WCO), 154.2, 153.7, 147.3, 145.3 (CH(CCH₃)₂), 108.3, 107.5 (CH(CCH₃)₂), 15.8, 15.0, 12.6, 12.3 ppm (CCH₃), the alkyne resonances are in coalescence).

UV/Vis (CH₂Cl₂): λ_{\max} (ϵ) = 334 (23700), 380 (10100), 470 (sh, 7900), 599 nm (43000 M⁻¹cm⁻¹).

2. Electrochemical data for 2 - 4 and reduction experiment with 3.

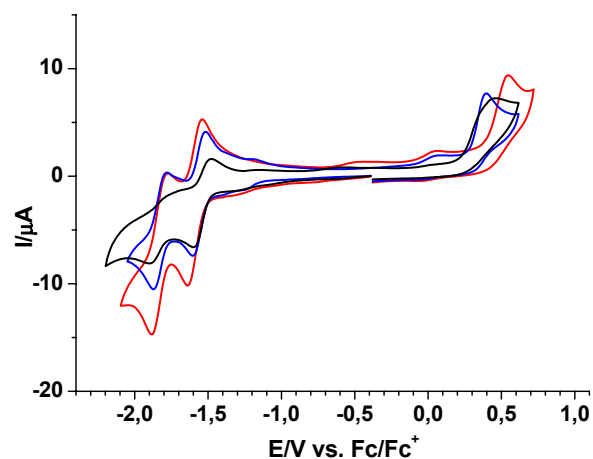


Figure S1. Cyclic voltammograms of [Ni(1)₂] 2 (black), [Pd(1)₂] 3 (red) and [Pt(1)₂] 4 (blue).

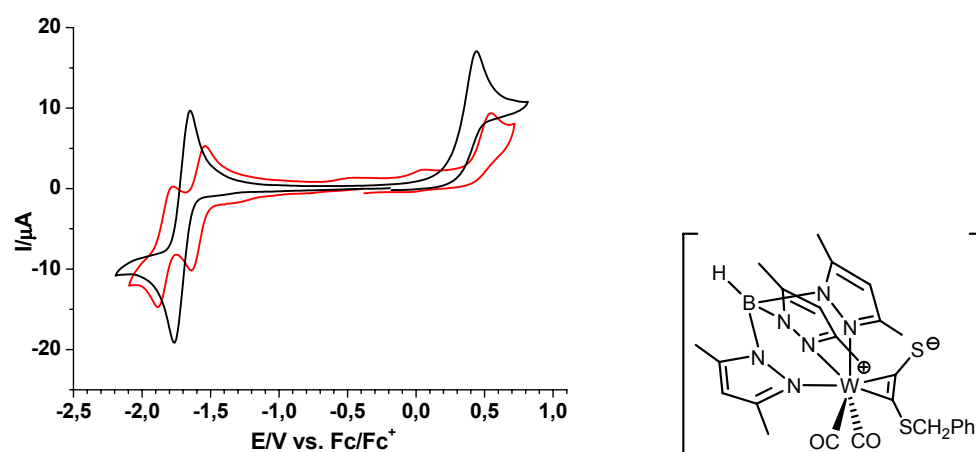


Figure S2. Cyclic voltammograms of [Pd(1)₂] 3 (red) and [Tp'W(CO)₂{η²-(BnS)CC(S)}] (black) for comparison.

One electron reduction of [Pd(1)₂] 3

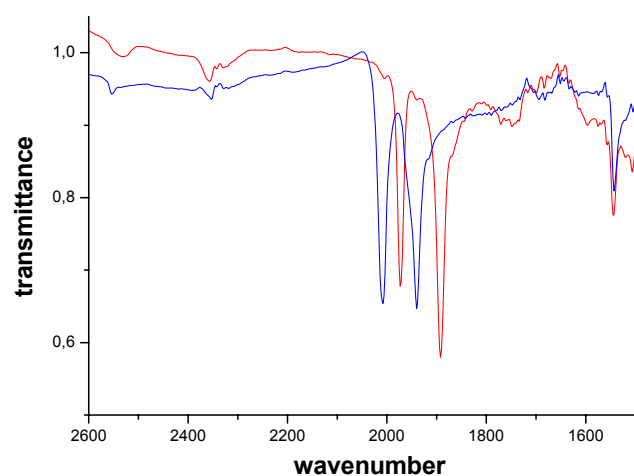


Figure S3. IR spectra of [Ni(1)₂] 2 before (blue) and after (red) reduction with one equivalent of C₈K in THF.

3. Reactivity of the Bis(metalla-acetylendithiolate)complexes 2 and 4.

Reaction of [Ni(1)₂] 2 with excess pyridine

Experimental: A blue solution of 3 mg [Ni(1)₂] 2 in 2 ml dichloromethane was treated with 100 µl pyridine. The solution turned yellow in the course of 12 hours. The IR band at 1543 cm⁻¹, which is indicative for the pyrazole ligand, serves as standard, the strong bands around 1600 cm⁻¹ are due to the excess of pyridine.

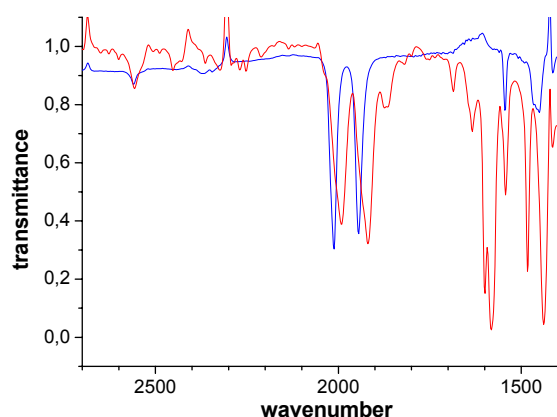


Figure S4. IR spectra of [Ni(1)₂] 2 before (blue) and after (red) addition of pyridine.

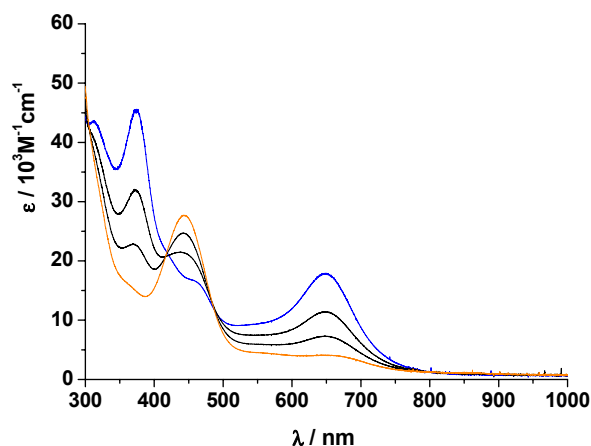


Figure S5. UV/vis spectroscopic monitoring of the reaction of [Ni(1)₂] 2 with excess pyridine in CH₂Cl₂, after 5 minutes (blue line), 5, 10 and 15 hours (red line).

Estimation of μ_{eff} by means of the EVANS-method:

5 mg [Ni(1)₂] 2 are solved in 2 ml CH₂Cl₂ and 300 µl d⁵-pyridine

$$\mu_{\text{eff}} = 2.828 \sqrt{\chi_m \cdot T} \quad \chi_m = \chi \cdot M - \chi_m(\text{dia}) \quad \chi = 3000 \cdot \Delta\nu / 4\pi \cdot \nu_0 \cdot c \cdot M$$

with $\Delta\nu = 14.4$ Hz; $\nu_0 = 400$ MHz; $c = 1.66 \cdot 10^{-3}$ mol/l, $M = 1309.11$ g·mol⁻¹, $T = 300$ K

diamagnetic correction: $\chi_m(\text{dia}) = 688 \cdot 10^{-6}$ cm³·mol⁻¹

$$\underline{\mu_{\text{eff}} = 3.28 \mu_B}$$