

## Supporting Information for:

# (Electro)catalytic C-C bond formation reaction with a redox-active cobalt complex

### Experimental section

#### General considerations

The ligand **H<sub>2</sub>L** was prepared according to reported procedure.<sup>S1</sup> All other reagents are commercially available and were used as received. All solvents were dried and distilled using common techniques unless otherwise mentioned. CoCl<sub>2</sub> was also dried by a literature known procedure.<sup>S2</sup> All reactions are carried out under a N<sub>2</sub>-atmosphere.

#### Instrumentation

Cyclic voltammetry was carried out in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> solution using a three-electrode configuration (Pt or glassy carbon working electrode, Pt counter electrode, Ag wire as pseudoreference) and PAR VersaSTAT 4 potentiostat. The ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) couple served as internal reference. Elemental analysis was performed on a Perkin Elmer Analyser 240. Mass spectrometry experiments were carried out on a Bruker Daltonics Microtof-Q mass spectrometer and mass spectrum simulations were done with mmass. X-ray diffraction measurement was done on a STOE X-Area diffractometer or a BRUKER Smart AXS diffractometer (graphite-monochromated Mo K $\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ). SHELXS-97 and SHELXL-97 were used to solve and refine the structure.<sup>S3</sup> CCDC 902892 contains the cif file for this manuscript. All these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_requests/cif](http://www.ccdc.cam.ac.uk/data_requests/cif)

#### Magnetic measurements

Samples were prepared by wrapping ca. 10 mg of the powdered complex with a small piece (ca. 1 cm<sup>2</sup>) of Teflon tape and pressing them into 5 mm pellets.

Temperature-dependent magnetic susceptibility measurements between 1.8 and 300 K were carried out in applied fields of 1000 Oe (below 50 K) and 10000 Oe (above 40K); field-dependent magnetization measurements were carried out at 1.8 K between 0 and 70000 Oe on a Quantum Design MPMS XL7 superconducting quantum interference (SQUID) magnetometer.

### EPR spectroscopy

X-band EPR spectra at different temperatures between 5 and 10 K were recorded on a Bruker EMX spectrometer equipped with a continuous flow cryostat. The microwave power was adjusted to values that did not cause saturation of the signals. The complexes were studied in solid state and as a frozen solution in a mixture of toluene and dichloromethane (1:1). Spectra were simulated by using Easyspin.<sup>S4</sup>

### Syntheses

**[1]:** The ligand **H<sub>2</sub>L** (711 mg, 4.08 mmol, 2.0 eq) was dissolved in Et<sub>2</sub>O, abs. (13 mL) and cooled to -95°C. Butyllithium (2.5 M in *n*-hexane, 2.0 mL, 4.6 eq) was added. To this solution a solution of CoCl<sub>2</sub> (262 mg, 2.04 mmol, 1.0 eq) in THF, abs. (27 mL) was added. The reaction mixture was stirred over night and was allowed to warm to room temperature. The oxidation was accomplished by passing a stream of pure oxygen through the solution for 10 min and stirring the resulting dark-green suspension for 1 h. The solvent was removed *in vacuo* and the residue was dissolved with *n*-hexane (60 mL). The solution was filtrated trough a cannula. The solvent was removed *in vacuo*. The resulting green solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and layered by MeOH (30 mL) and storred at -20°C for four days. Single crystals could be obtained by this method. Yield: 220 mg (15%). HRMS (ESI): calc for C<sub>48</sub>H<sub>52</sub>N<sub>4</sub>Co (M<sup>+</sup>): *m/z* 743.35, found: 743.35. Anal. Calc. for C<sub>48</sub>H<sub>52</sub>N<sub>4</sub>Co ·0.95 CH<sub>2</sub>Cl<sub>2</sub>: C 71.30; H 6.59; N 6.79 %; found: C 71.45; H 6.58; N 6.39 %.

**Table S1.** Crystallographic details for **1**•CH<sub>2</sub>Cl<sub>2</sub>.

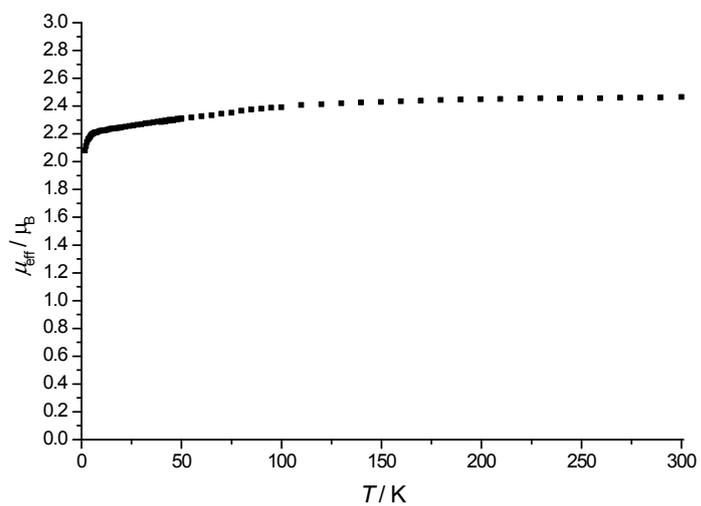
	<b>1</b> •CH <sub>2</sub> Cl <sub>2</sub>
Chemical formula	C <sub>49</sub> H <sub>52</sub> Cl <sub>2</sub> Co N <sub>4</sub>
<i>M<sub>r</sub></i>	826.78
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n
<i>a</i> (Å)	11.729(5)
<i>b</i> (Å)	14.574(5)
<i>c</i> (Å)	25.358(5)
<i>α</i> (°)	90.000(5)
<i>β</i> (°)	95.532(5)
<i>γ</i> (°)	90.000(5)
<i>V</i> (Å <sup>3</sup> )	4314.47(3)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.273
Temperature (K)	200(2)
<i>μ</i> (mm <sup>-1</sup> )	0.560
Crystal size (mm)	0.30 x 0.20 x 0.06
K $\alpha$	0.71073 (Mo)
F(000)	1740
meas./ indep. refl.	55567/11653
obsvd. [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	6501
refl.	
R <sub>int</sub>	0.1200
R[ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )]	0.0673
wR ( <i>F</i> <sup>2</sup> )	0.1609
<i>S</i>	0.963
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.443, -0.525

**Table S2.** Selected bond lengths (Å) and bond angles (°) of **1**•CH<sub>2</sub>Cl<sub>2</sub>.

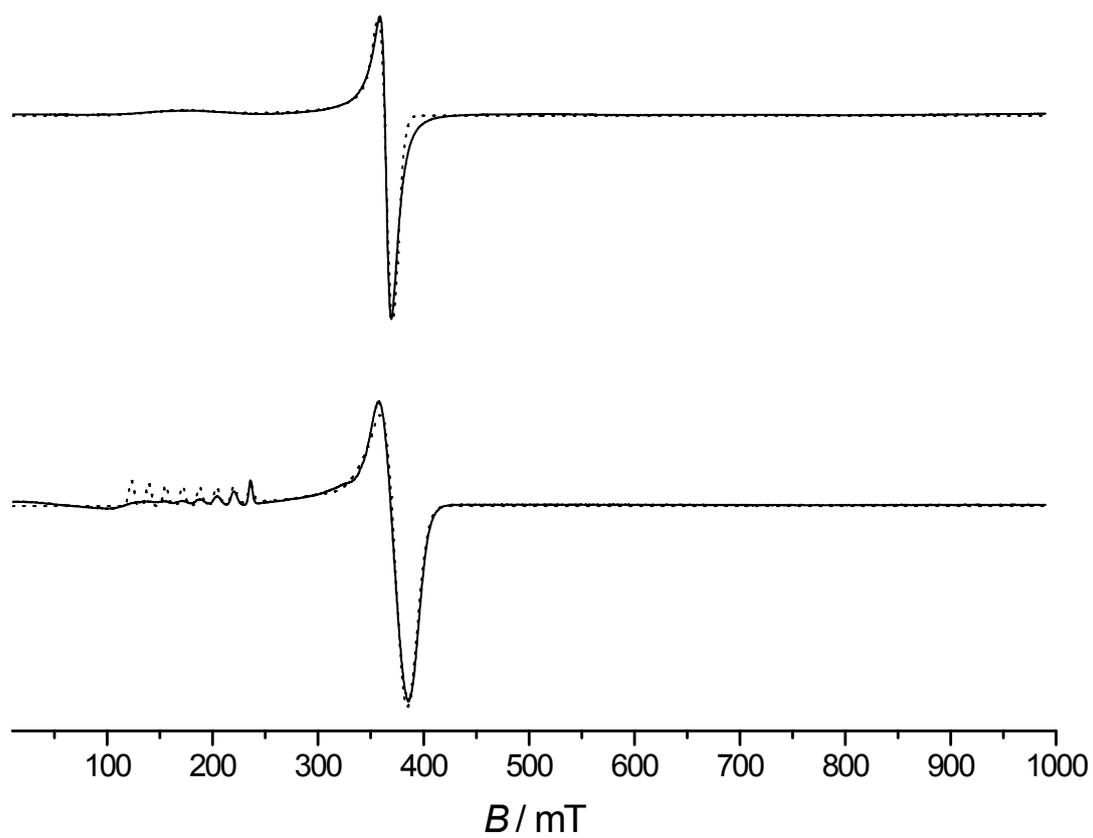
<b>Co - N1</b>	1.9223(3)	<b>C1A - C2A</b>	1.4234(4)
<b>Co - N1A</b>	1.9202(3)	<b>C2A - C3A</b>	1.4163(5)
<b>Co - N2</b>	1.9180(3)	<b>C3A - C4A</b>	1.3745(5)
<b>Co - N2A</b>	1.9265(3)	<b>C4A - C5A</b>	1.4062(5)
<b>C1 - C2</b>	1.4313(5)	<b>C5A - C6A</b>	1.3610(6)
<b>C2 - C3</b>	1.4168(5)	<b>C6A - C1A</b>	1.4179(4)
<b>C3 - C4</b>	1.3726(5)	<b>N1 - C16</b>	1.4365(4)
<b>C4 - C5</b>	1.4093(6)	<b>N2 - C7</b>	1.4317(4)
<b>C5 - C6</b>	1.3768(5)	<b>N1A - C16A</b>	1.4379(4)
<b>C6 - C1</b>	1.4116(5)	<b>N2A - C7A</b>	1.4349(4)

<b>N1 - Co - N2</b>	83.8 (3)	<b>N1 - Co - N2A</b>	106.3 (1)
<b>N1A - Co - N2A</b>	83.8 (1)	<b>N2 - Co - N1A</b>	105.0 (1)
<b>N1 - Co - N1A</b>	146.5 (8)	<b>N2 - Co - N2A</b>	147.3(1)

## SQUID Magnetometry and EPR Spectroscopy

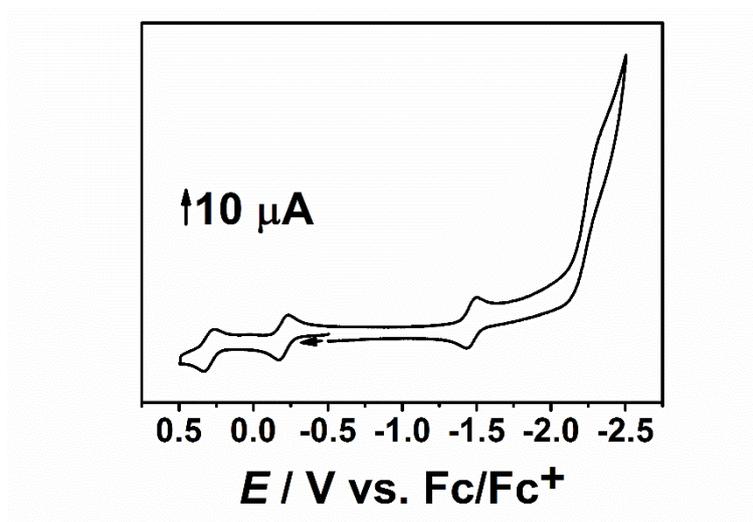


**Fig. S1**  $\mu_{eff}$  as a function of  $T$  for complex **1** measured at  $H = 0.1$  T (below 50 K) and  $H = 1$  T (above 40 K).

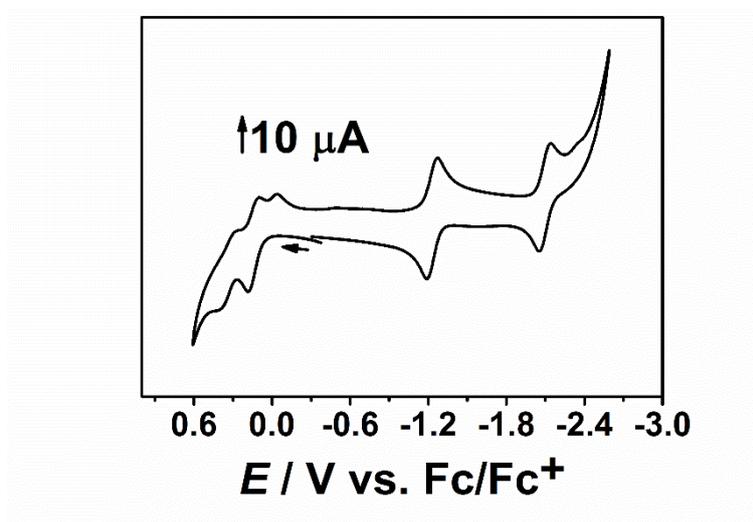


**Fig. S2** X-band EPR spectra of solid **1** and a frozen solution of **1** in a mixture of dichloromethane and toluene (1/1) at 5 K. Solid lines: Experimental spectra, dashed lines: Best fits.

## Cyclic voltammetry



**Fig. S3** Cyclic voltammogram of **1**. Conditions:  $\text{CH}_2\text{Cl}_2$  / 0.1 M  $\text{Bu}_4\text{NPF}_6$ , 298 K and scan rate  $100 \text{ mV s}^{-1}$ .

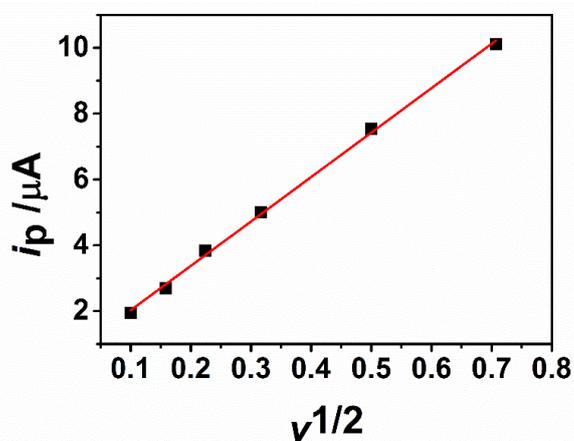
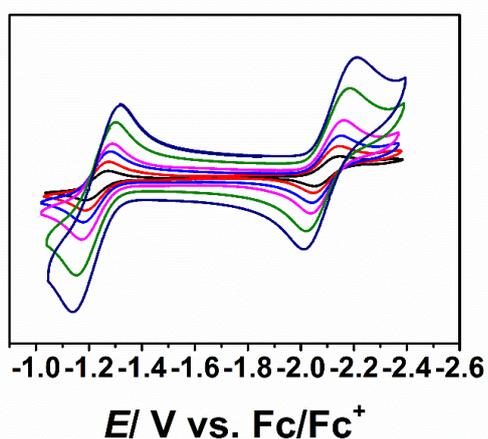


**Fig. S4** Cyclic voltammogram of **1**. Conditions: THF / 0.1 M  $\text{Bu}_4\text{NPF}_6$ , 298 K and scan rate  $100 \text{ mV s}^{-1}$ .

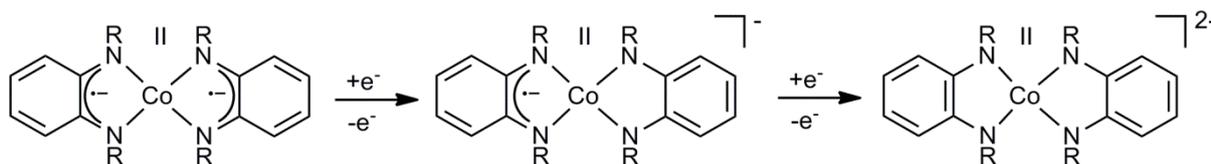
**Table S3.** Electrochemical data from cyclic voltammetry<sup>a</sup>

Solvent	$E^{\text{ox}2} / \text{V}$	$E^{\text{ox}1} / \text{V}$	$E^{\text{red}1} / \text{V}$	$E^{\text{red}2} / \text{V}$
THF	0.40	0.19	-1.23	-2.10
CH <sub>2</sub> Cl <sub>2</sub>	0.30	-0.21	-1.47	-

<sup>a</sup>Half-wave potentials from cyclic voltammetric measurements in THF or CH<sub>2</sub>Cl<sub>2</sub>, 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> for reversible processes at 298 K, scan rate 100 mV s<sup>-1</sup>, ferrocene/ferrocenium was used as an internal standard.



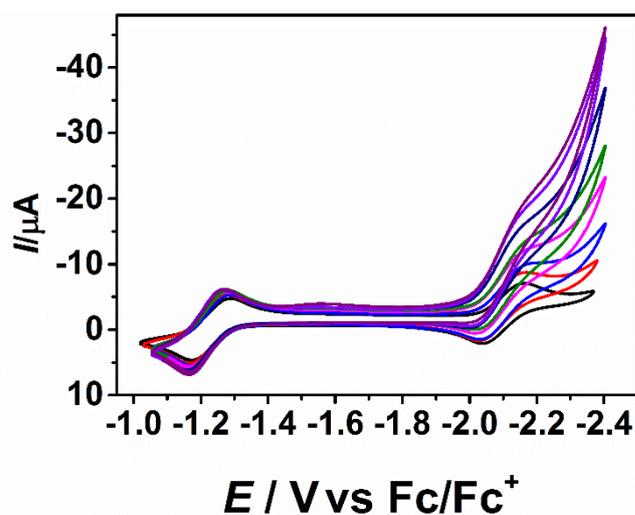
**Fig. S5** Top: Cyclic voltammogram of **1**. Conditions: THF / 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>, 298 K and scan rate 10 - 500 mV s<sup>-1</sup>. Bottom: Plot  $i_p$  vs  $v^{1/2}$ . A linear plot indicates the reaction is under diffusion control.

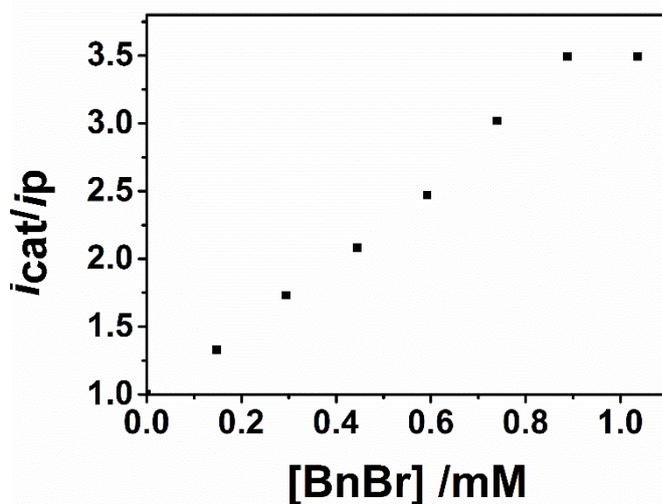


**Scheme S1.** Proposed mechanism for electrontransfer **1**.

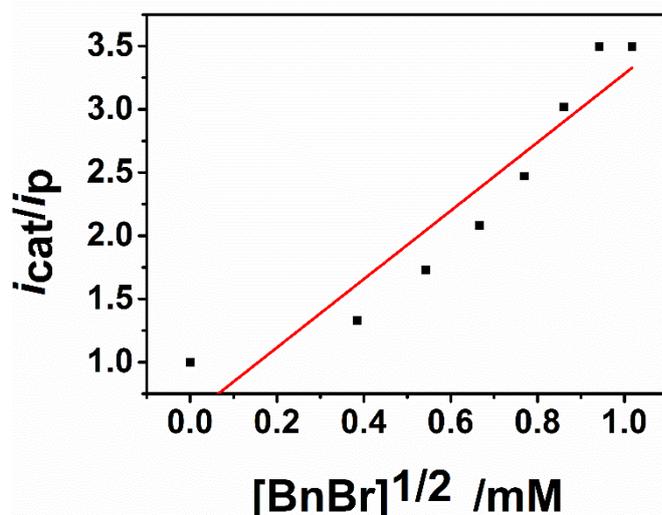
### Cyclic voltammetry experiment in presence of benzyl bromide

Under nitrogen atmosphere **1** (1.1 mg, 1.48  $\mu\text{mol}$ ) was dissolved in degassed THF, 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> solution (5 mL). Benzylbromide solution (0.12  $\mu\text{L}$ , 0.74  $\mu\text{mol}$ , 4  $\mu\text{L}$  THF) was added to the green solution of the complex. After the addition of the benzyl bromide solution a cyclic voltammogram was recorded. The addition was repeated seven times to increase the concentration of benzyl bromide. After every addition a cyclic voltammogram was recorded.

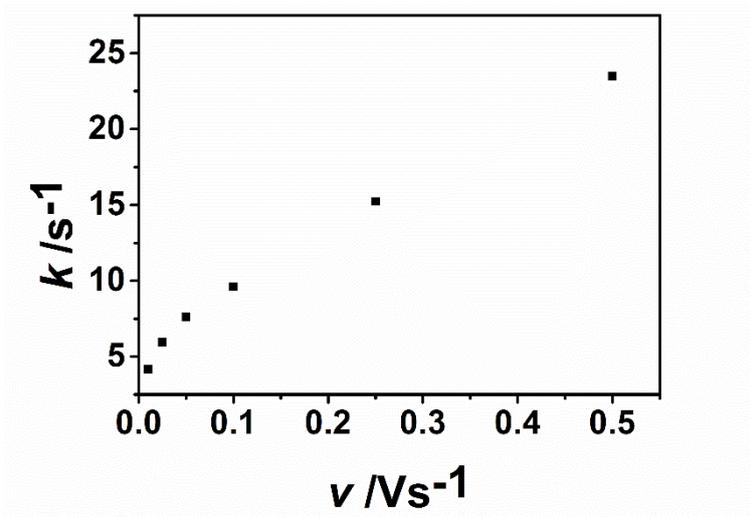




**Fig. S6** Top: Cyclic voltammogram of a solution of **1** and benzyl bromide. Conditions: glassy carbon working electrode, 71 mm<sup>2</sup>, THF, 0.29 x 10<sup>-3</sup> M **1**, 0.15 x 10<sup>-3</sup> M to 1.02 x 10<sup>-3</sup> M benzyl bromide, 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>, and scan rate 100 mVs<sup>-1</sup>. Bottom: Plot  $i_{cat}/i_p$  vs [BnBr].



**Fig. S7** A plot of  $i_{cat}/i_p$  versus the square root of BnBr concentration (from 0.15 x 10<sup>-3</sup> M to 1.02 x 10<sup>-3</sup> M) for a 0.29 x 10<sup>-3</sup> M solution of **1** (100 mVs<sup>-1</sup> scan rate). The linear relationship between  $i_{cat}/i_p$  versus the square root of base concentration suggests the catalytic rate is first order in BnBr concentration.

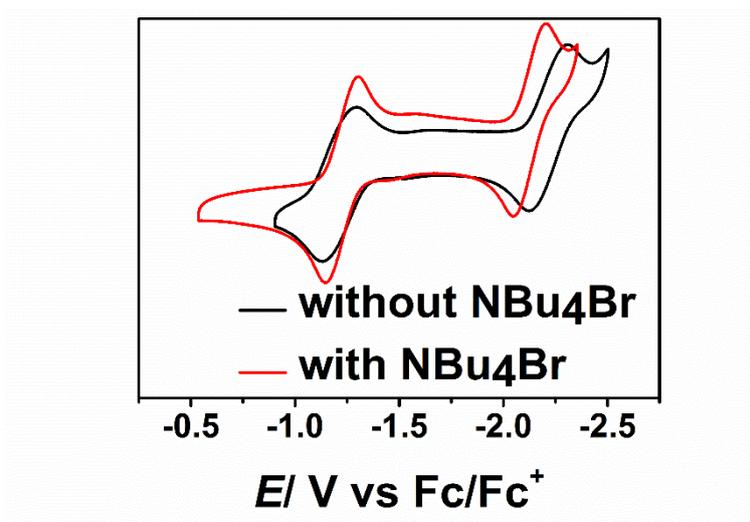


**Fig. S8** A plot of  $k_{obs}$  versus the scan rate  $v$  indicates that  $k_{obs}$  has a linear dependence on  $v$ .

$$\frac{i_{cat}}{i_p} = \frac{n}{0.4463} \cdot \sqrt{\frac{RTk_{obs}}{F \cdot v}}$$

$k_{obs}$  = turnover frequency

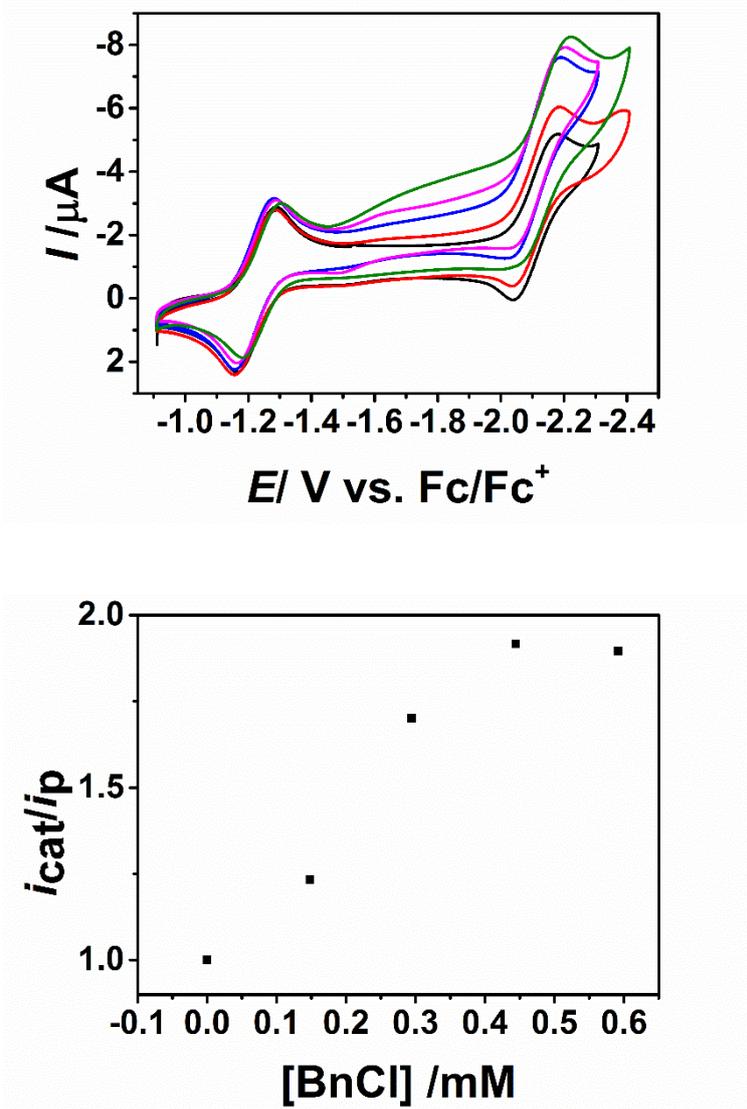
$n$  = number of electrons



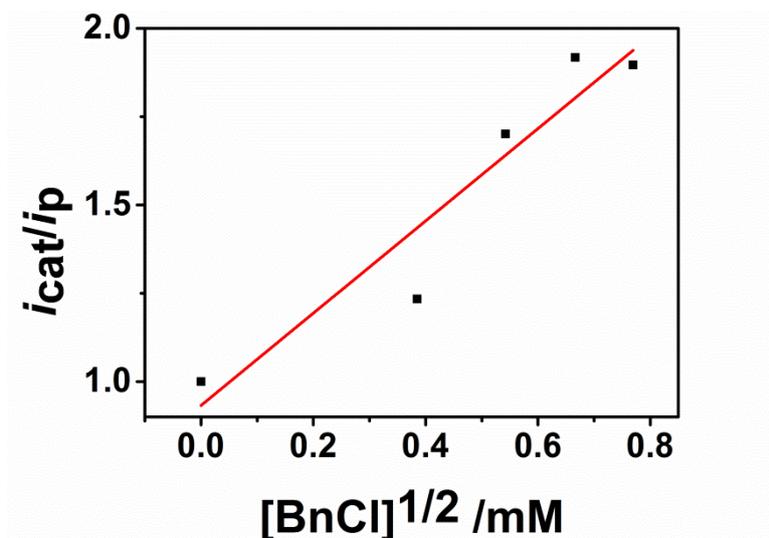
**Fig. S9** Cyclic voltammogram of **1** in the presence and absence of  $NBu_4Br$ .

**Cyclic voltammetry experiment in presence of benzyl chloride**

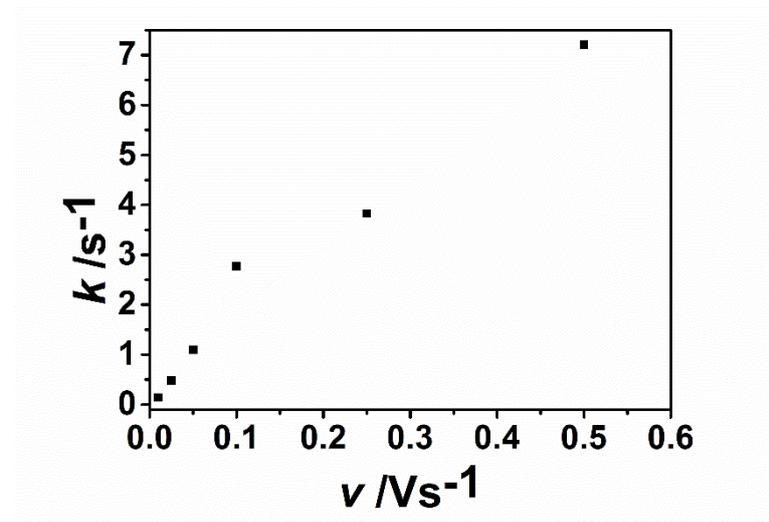
Under nitrogen atmosphere **1** (1.1 mg, 1.48  $\mu\text{mol}$ ) was dissolved in degassed THF, 0.1 M  $\text{Bu}_4\text{NPF}_6$  solution (5 mL). Benzyl chloride solution (0.08  $\mu\text{L}$ , 0.74  $\mu\text{mol}$ , 4  $\mu\text{L}$  THF) was added to the green solution of the complex. After the addition of the benzyl chloride solution a cyclic voltammogram was recorded. The addition was repeated four times to increase the concentration of benzyl chloride. After every addition a cyclic voltammogram was recorded.



**Fig. S10** Top: Cyclic voltammogram of a solution of **1** and benzylchloride. Conditions: glassy carbon working electrode, 71  $\text{mm}^2$ , THF,  $0.29 \times 10^{-3}$  M **1**,  $0.15 \times 10^{-3}$  M to  $0.60 \times 10^{-3}$  M benzylchloride, 0.1 M  $\text{Bu}_4\text{NPF}_6$ , and scan rate  $100 \text{ mVs}^{-1}$ . Bottom: Plot  $i_{\text{cat}}/i_p$  vs  $[\text{BnCl}]$ .



**Fig. S11** A plot of  $i_{cat}/i_p$  versus the square root of BnCl concentration (from  $0.15 \times 10^{-3}$  M to  $0.60 \times 10^{-3}$  M) for a  $0.29 \times 10^{-3}$  M solution of **1** ( $100 \text{ mVs}^{-1}$  scan rate). The linear relationship between  $i_{cat}/i_p$  versus the square root of base concentration suggests the catalytic rate is first order in BnCl concentration.



**Fig. S12** A plot of  $k_{obs}$  versus the scan rate  $v$  indicates that  $k_{obs}$  has a linear dependence on  $v$ .

$$\frac{i_{cat}}{i_p} = \frac{n}{0.4463} \cdot \sqrt{\frac{RTk_{obs}}{F \cdot v}}$$

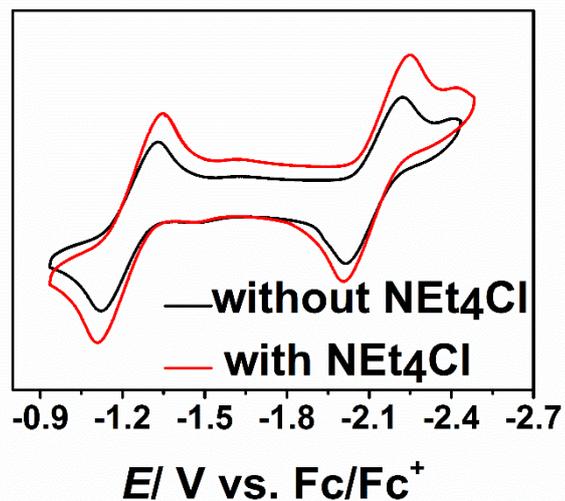
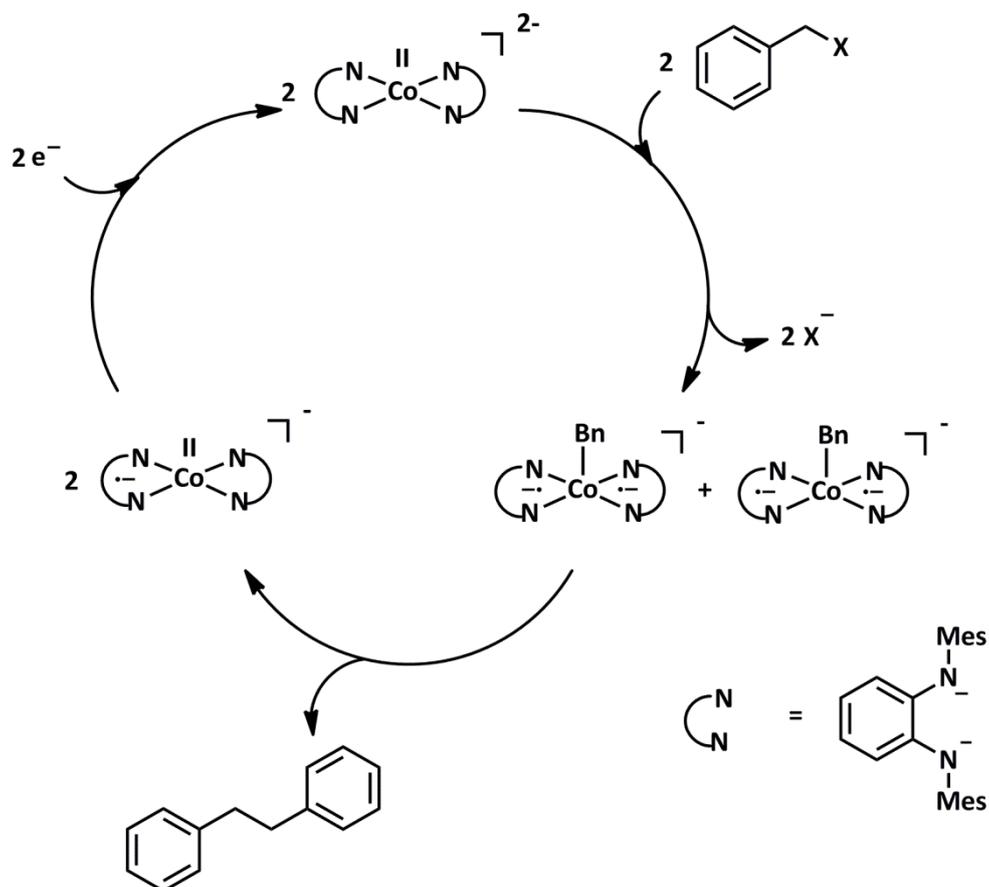


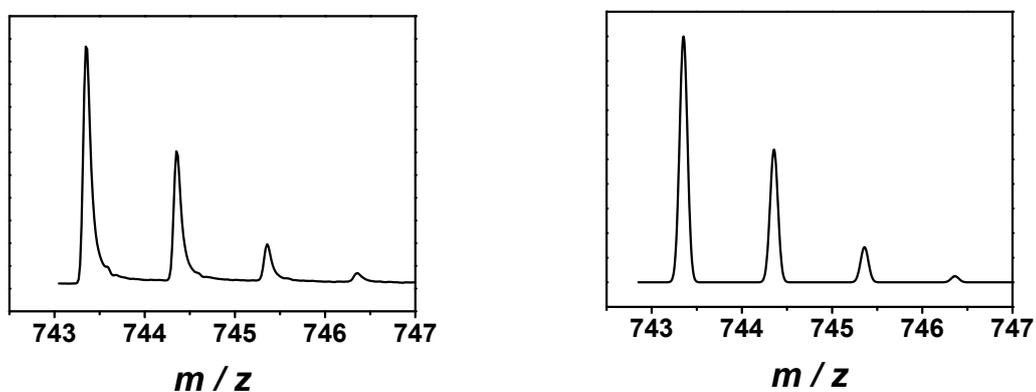
Fig. S13 Cyclic voltammogram of **1** in the presence and absence of  $\text{NEt}_4\text{Cl}$ .



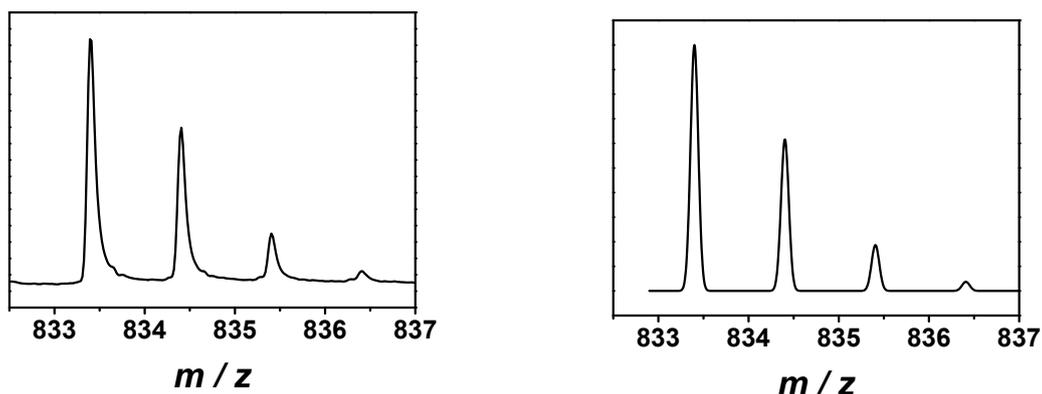
Scheme S2 Postulated Mechanism for Activation of Benzylbromide or Benzylchloride

### Intermediates of the postulated mechanism

The Ligand **H<sub>2</sub>L** (50 mg, mmol, 2.0 eq) was dissolved in Et<sub>2</sub>O, abs. (5 mL) and cooled to -90°C. Butyllithium (2.5 M in *n*-hexane, 0.2 mL, 4.6 eq) was added. To this solution a solution of CoCl<sub>2</sub> (20 mg, 2.04 mmol, 1.0 eq) in THF, abs. (10 mL) was added. The reaction mixture was stirred over night and was allowed to warm to room temperature. Benzyl chloride was added and the solution was frozen and carried to the ESI-MS. There it was allowed to warm to room temperature, the solution was deconcentrated by addition of THF and a spectrum was taken immediately.



**Fig. S14** Mass spectrum of **1** (left) and simulated mass spectrum of **1** (right)

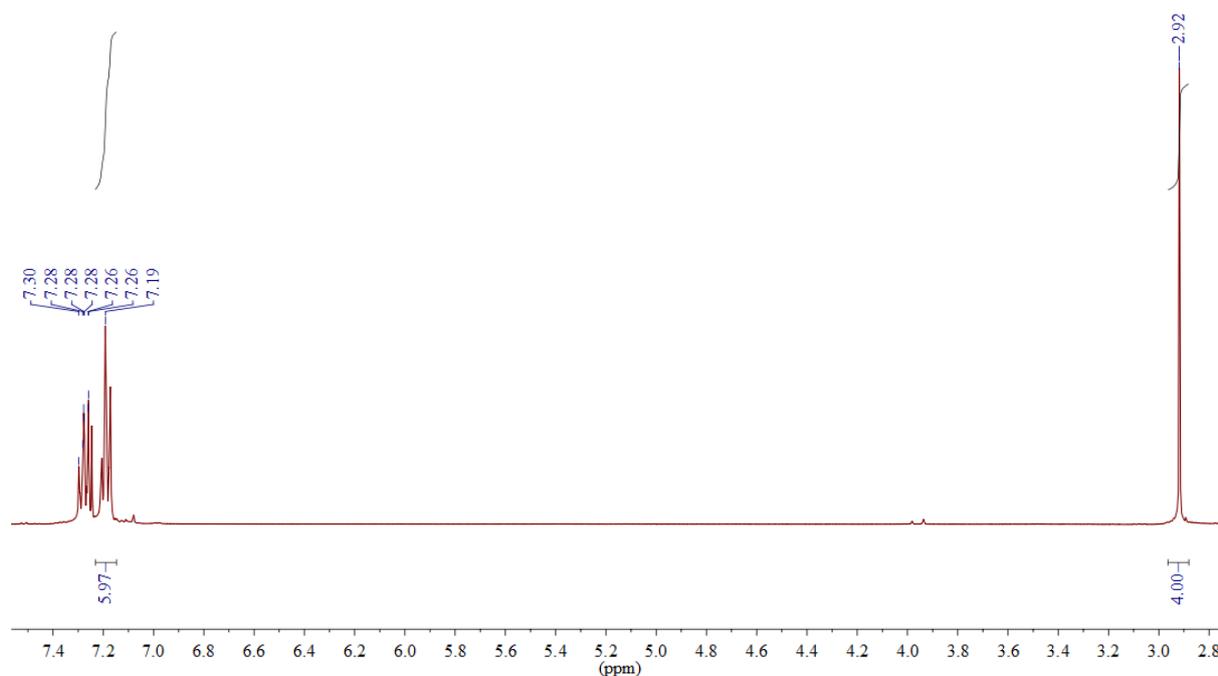


**Fig. S15** Mass spectrum of **1** + CH<sub>2</sub>Ph-H (left) and simulated mass spectrum of **1**+ CH<sub>2</sub>Ph-H (left)

### Isolation of the product

The Ligand H<sub>2</sub>L (166 mg, 0.95 mmol, 2.0 eq) was dissolved in Et<sub>2</sub>O, abs. (3 mL) and cooled to -90°C. Butyllithium (2.5 M in *n*-hexane, 0.4 mL, 4.0 eq) was added. To this solution a solution of CoCl<sub>2</sub> (61 mg, 0.48 mmol, 1.0 eq) in THF, abs. (6 mL) was added. The reaction mixture was stirred overnight and was allowed to warm to room temperature. Benzyl bromide (70 μL, 0.58, 1.2 eq) was added and the solution was stirred overnight. Water was added and the aqueous phase was extracted with Et<sub>2</sub>O (3 x 10 mL). The combined organic layers were dried with Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed *in vacuo*. The residue was purified by column chromatography (Silica, pentane: CH<sub>2</sub>Cl<sub>2</sub>; 9:1) to yield a colorless oil in 80 % yield.

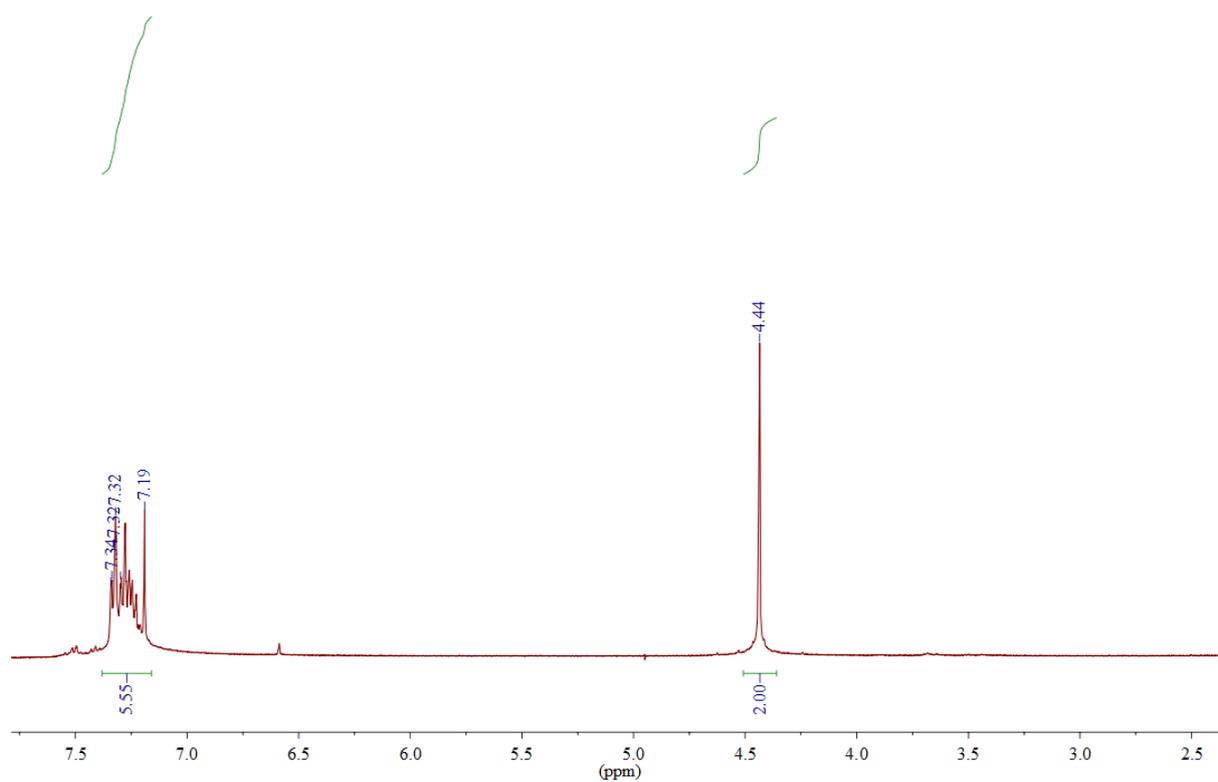
<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>): δ [ppm] = 7.30 – 7.25 (m, 4 H, Ph), 7.21 -7.17 (m, 6 H, Ph), 2.92 (s, 4 H, CH<sub>2</sub>).



**Fig. S16** <sup>1</sup>H-NMR of bibenzyl.

$\text{CoCl}_2$  (143 mg, 1.1 mmol, 1 eq) was dissolved in THF, abs. (20 mL) and benzyl bromide (0.13 mL, 1.1 mmol, 1 eq) was added. The resulting solution was stirred overnight at room temperature. Water (20 mL) was added and the aqueous layer was extracted with  $\text{Et}_2\text{O}$  (2 x 10 mL). The combined organic layers were dried with  $\text{Na}_2\text{SO}_4$  and the solvent was removed *in vacuo*. A  $^1\text{H-NMR}$ -spectrum was recorded in  $\text{CDCl}_3$ . Only the starting material benzyl bromide was detected.

$^1\text{H-NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 7.19 - 7.34 (m, 5 H, Ph), 4.44 (s, 2 H,  $\text{CH}_2$ ).



**Fig. S17**  $^1\text{H-NMR}$  of benzyl bromide.

**References:**

S1 V. M. Jiménez-Pérez, M. Ibarra-Rodríguez, B. M. Muñoz-Flores, A. Gómez, R. Santillan, E. Hernández Fernández, S. Bernès, N. Waksman and R. Ramírez Duron, *J. Mol. Struct.* 2013, **1031**, 168.

S2 H. Hecht, *Z. Anorg. Chem.*, 1947, **254**, 37.

S3 (a) G. M. Sheldrick, *Acta Crystallogr., Sect. A* 2008, **A64**, 112-122. (b) G. M. Sheldrick, *Program for Crystal Structure Solution and Refinement*, University of Göttingen: Göttingen, Germany, 1997.

S4 S. Stoll and A. Schweiger, *EasySpin, a comprehensive software package for spectral simulation and analysis in EPR*; *J. Magn. Reson.* 2006, **178(1)**, 42.