Electronic Supplementary Material (ESI) for Dalton Transactions.
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Supporting Information

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Table of Contents

Table S1: Crystal and structure refinement data for complexes **(1)** and **(2)**.....2

Figure S1: ^{1}H NMR spectrum of the complex **(1)** in DCM.....4

Figure S2: ^{31}P NMR spectrum of the complex **(1)** in DCM.....5

Figure S3: ^{1}H NMR spectrum of the complex **(2)** in DCM.....6

Figure S4: ^{31}P NMR spectrum of the complex **(2)** in DCM.....7

Figure S5: ESI-MS of complex **(1)** in MeOH.....8

Figure S6: ESI-MS of complex **(2)** in MeOH.....9

Figure S7: Calibration line used for CPC experiments.....10

Figure S8: Cyclic voltammogram of **[**Ni(xbSmS)] in MeCN.....11

Figure S9: Cyclic voltammogram of **[**Ni(xbSmSe)] in MeCN.....11

Figure S10: Cyclic voltammogram of [Ni(xbSmS)] with increasing concentration of HOAc.....12

Figure S11: Cyclic voltammogram of [Ni(xbSmSe)] with increasing concentration of HOAc.....12

Figure S12: Cyclic voltammogram of **[**$RuCp(PPh_3)(MeCN)_2]PF_6$ in MeCN.....13

Figure S13: Cyclic voltammogram of **[**$RuCp(PPh_3)(MeCN)_2]PF_6$ with increasing concentration of HOAc.....13

Table S1: Crystal and structure refinement data for complexes **(1)** and **(2)**

Data were collected at 110 K using a SuperNova, Dual, Cu at zero, Atlas. H-atom parameters were constrained.

	(1)	**(2)**
Crystal data		
Chemical formula	$2(C_{39}H_{44}NiPRuS_4)\cdot 2(F_6P)\cdot C_5H_{12}$	$2(C_{39}H_{44}NiPRuS_2Se_2)\cdot 2(F_6P)\cdot C_5H_{12}$
M_r	2025.54	2213.14
Crystal system, space group	Triclinic, $P-1$	Triclinic, $P-1$
a, b, c (Å)	10.4124 (3), 13.6997 (3), 16.9554 (5)	10.4311 (2), 13.7933 (3), 17.0273 (3)
α, β, γ (°)	71.664 (2), 86.558 (2), 69.587 (2)	71.685 (2), 86.5782 (17), 69.258 (2)
V (Å^3)	2148.30 (11)	2171.35 (8)
Z	1	1
Radiation type	Cu $K\alpha$	Cu $K\alpha$
μ (mm^{-1})	6.39	7.34
Crystal size (mm)	0.23 × 0.17 × 0.02	0.17 × 0.13 × 0.03
Data collection		
Absorption correction	Analytical *CrysAlis PRO*, Agilent Technologies, Version 1.171.36.32 (release 02-08-2013 CrysAlis171 .NET) (compiled Aug 2 2013,16:46:58) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897)[1]	Analytical *CrysAlis PRO*, Agilent Technologies, Version 1.171.36.32 (release 02-08-2013 CrysAlis171 .NET) (compiled Aug 2 2013,16:46:58) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897)[1]
T_{min}, T_{max}	0.436, 0.866	0.408, 0.833
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	27501, 8405, 7525	27022, 8480, 7577
R_{int}	0.039	0.033
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.617	0.616

$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.028, 0.073, 1.03	0.029, 0.074, 1.06
No. of reflections	8405	8480
No. of parameters	731	719
No. of restraints	875	851
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.57, -0.57	0.64, -0.61

Computer programs: *CrysAlis PRO*, Agilent Technologies, Version 1.171.36.32 (release 02-08-2013 CrysAlis171 .NET) (compiled Aug 2 2013, 16:46:58), *SHELXS2014*/7 (Sheldrick, 2015), *SHELXL2014*/7 (Sheldrick, 2015), *SHELXTL* v6.10 (Sheldrick, 2008).[2]

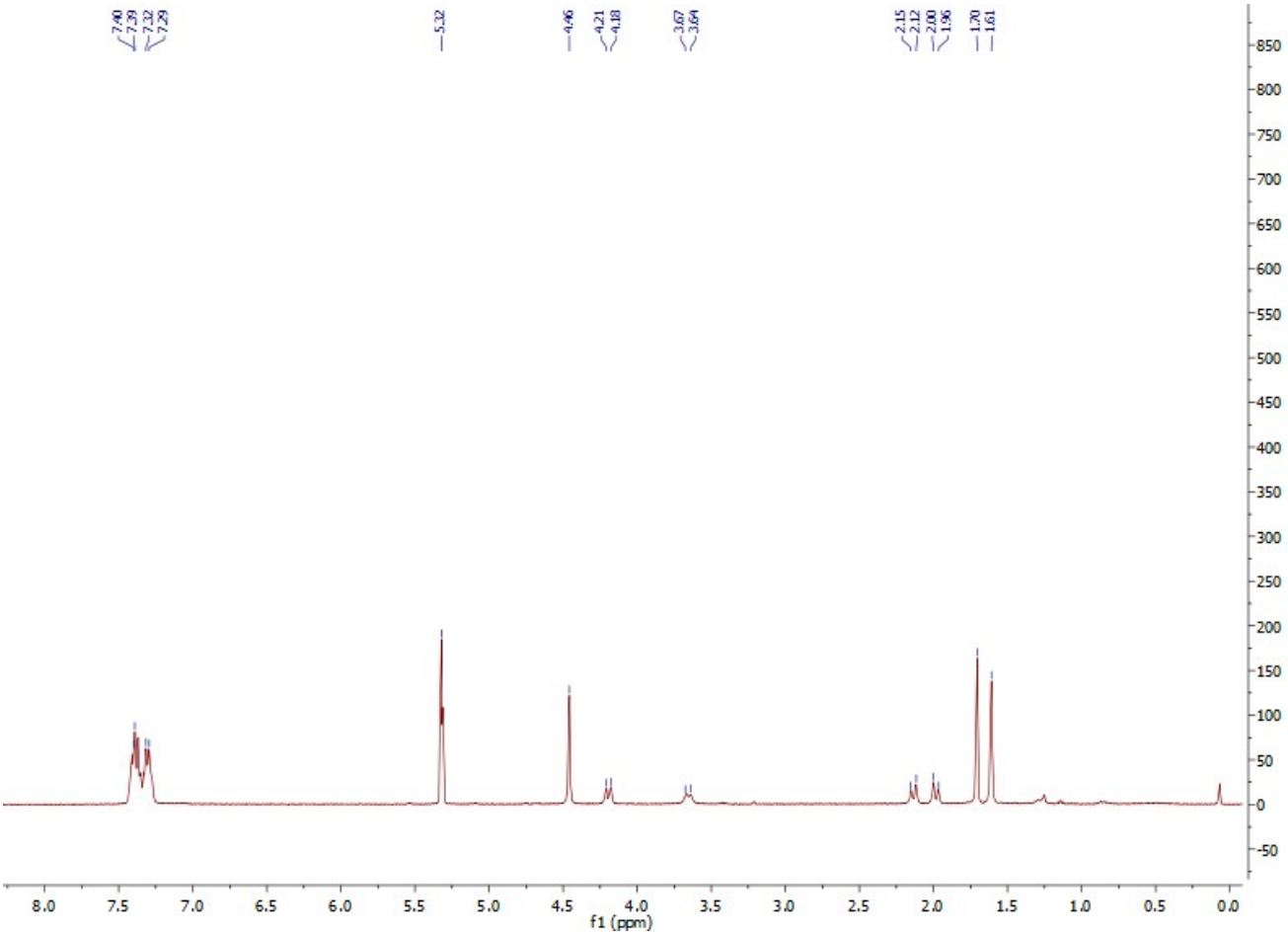

Figure S1: ^{1}H NMR spectrum of complex **(1)** in DCM.

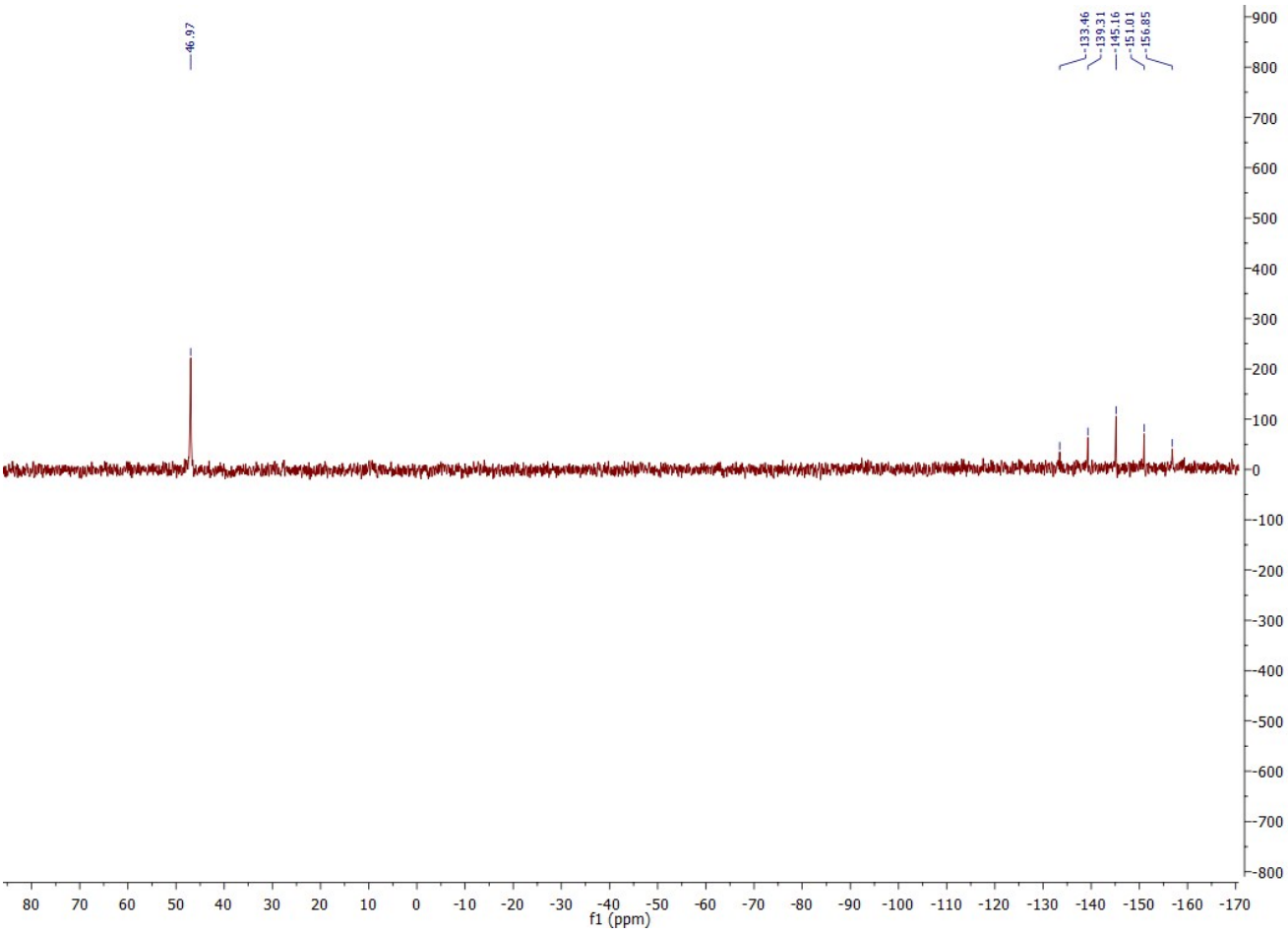

Figure S2: ^{31}P NMR spectrum of complex **(1)** in DCM.

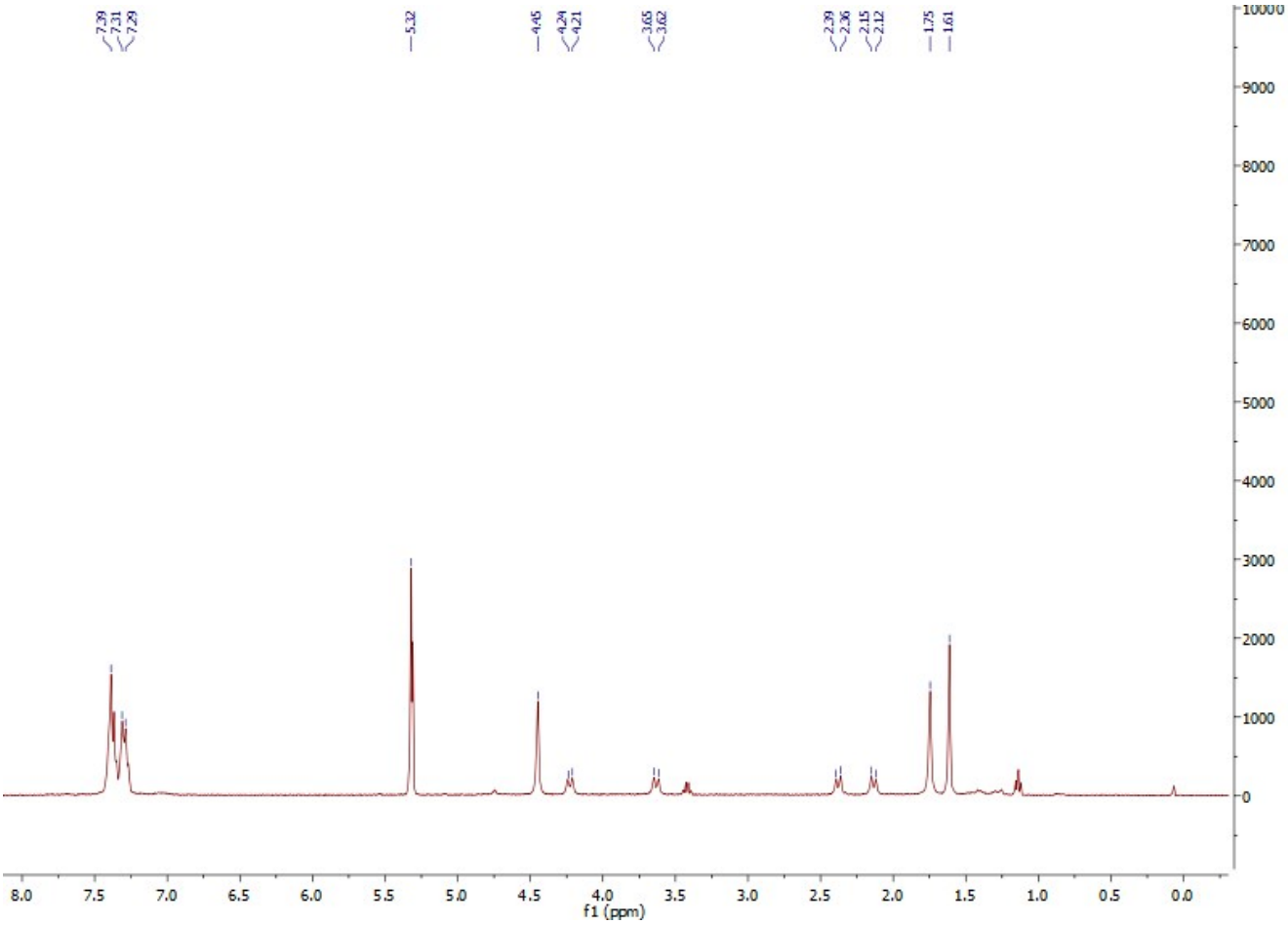

Figure S3: ^{1}H NMR spectrum of complex **(2)** in DCM.

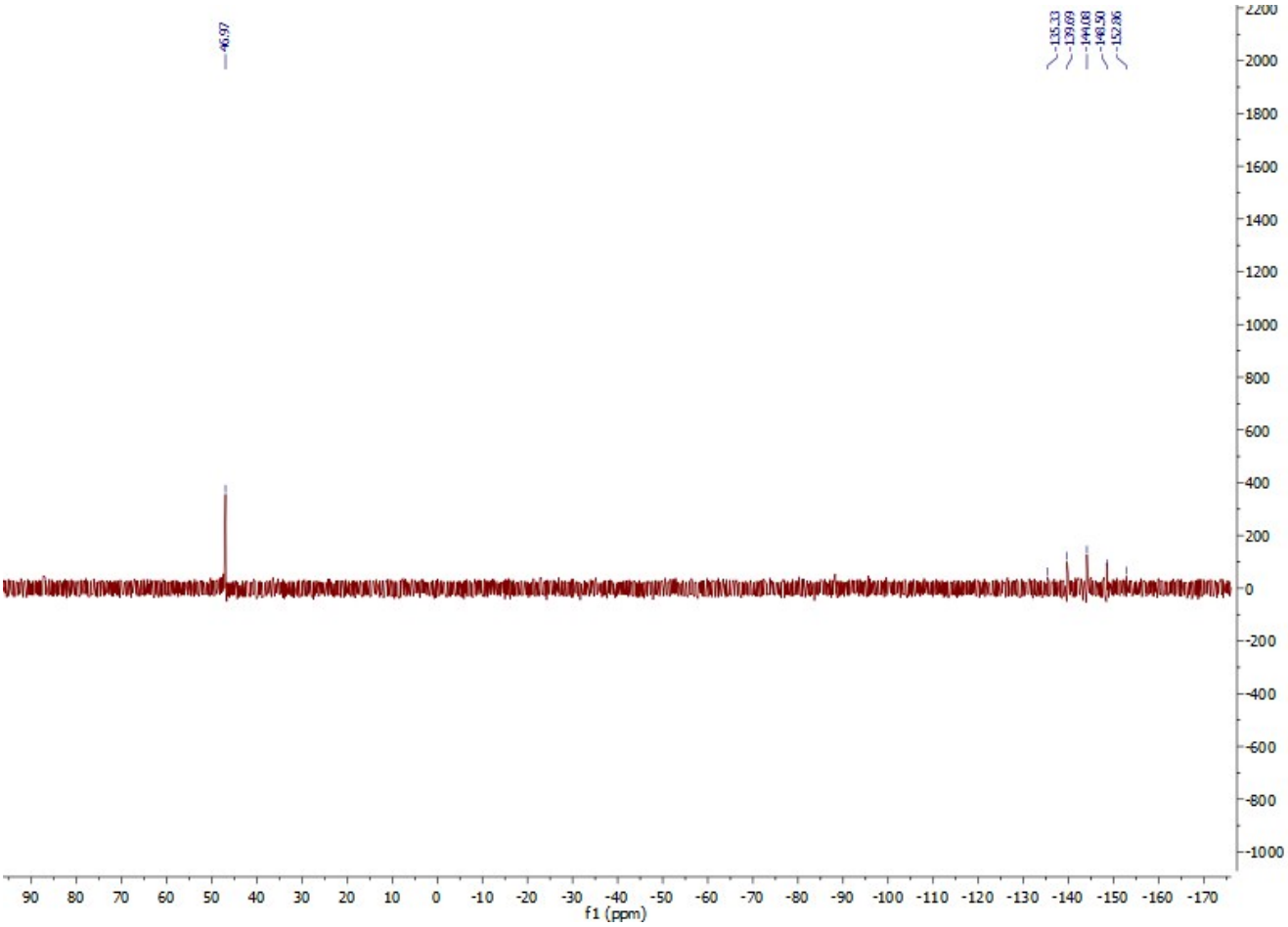

Figure S4: ^{31}P NMR spectrum of the complex **(2)** in DCM.

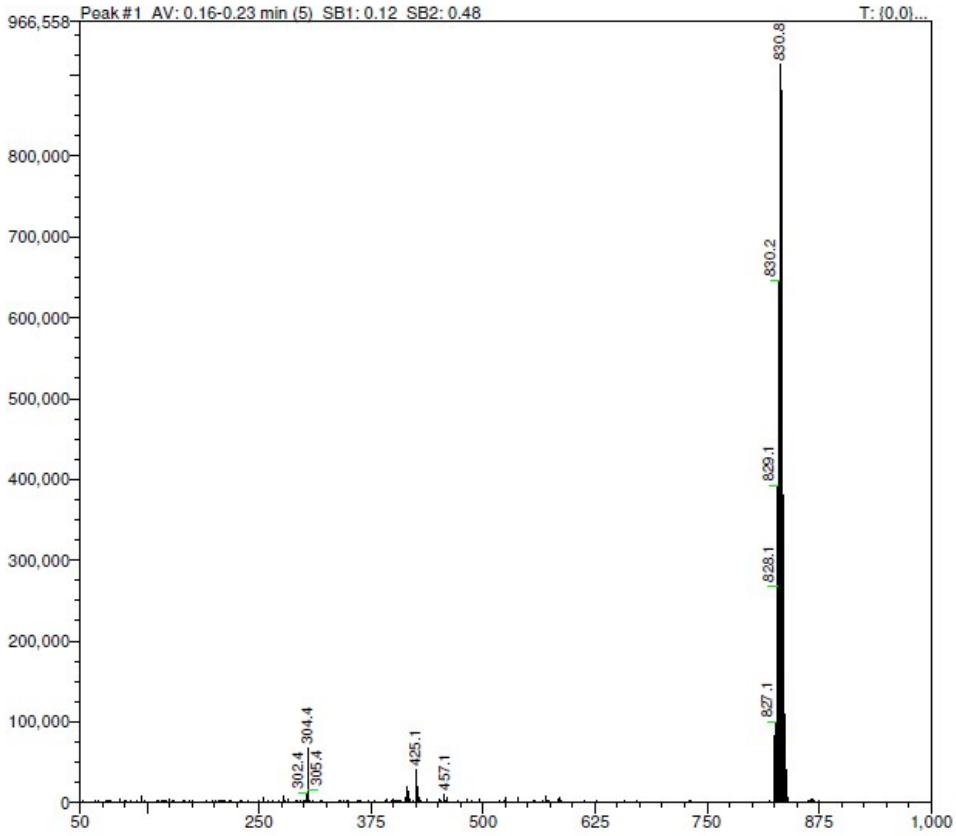

Figure S5: ESI-MS of complex **(1)** in MeOH 830.8, calcd: 831.0 $[M-PF_6]^+$.

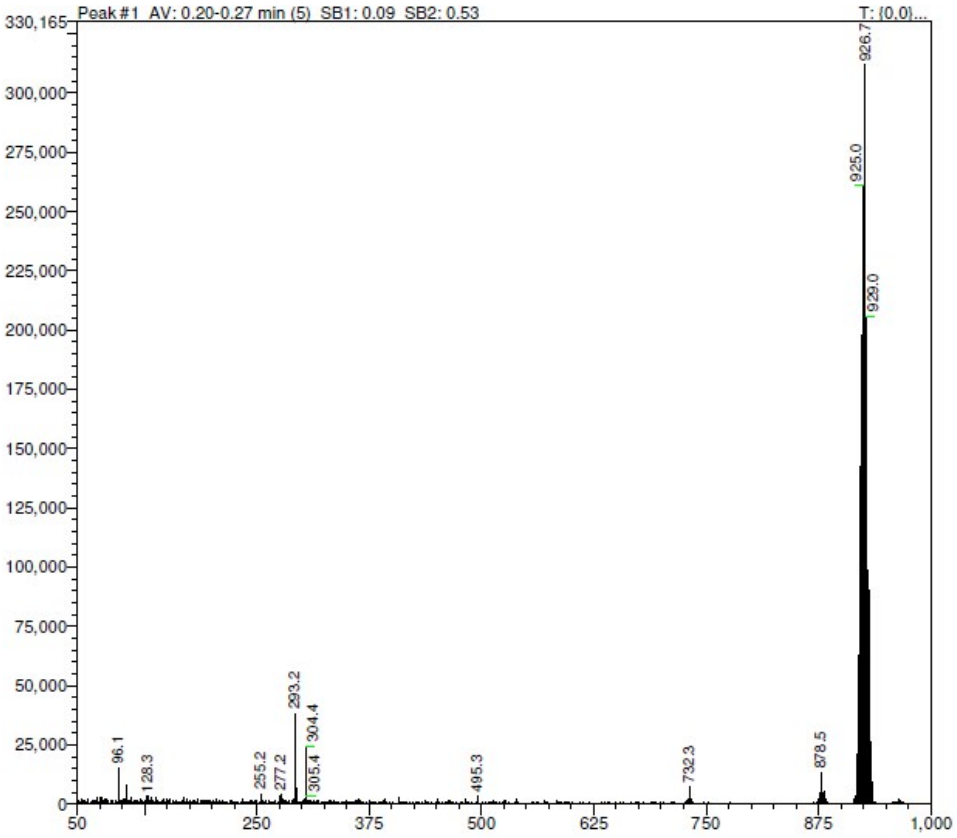

Figure S6: ESI-MS of complex **(2)** in MeOH 926.7, calcd: 926.9 $[M-PF_6]^+$.

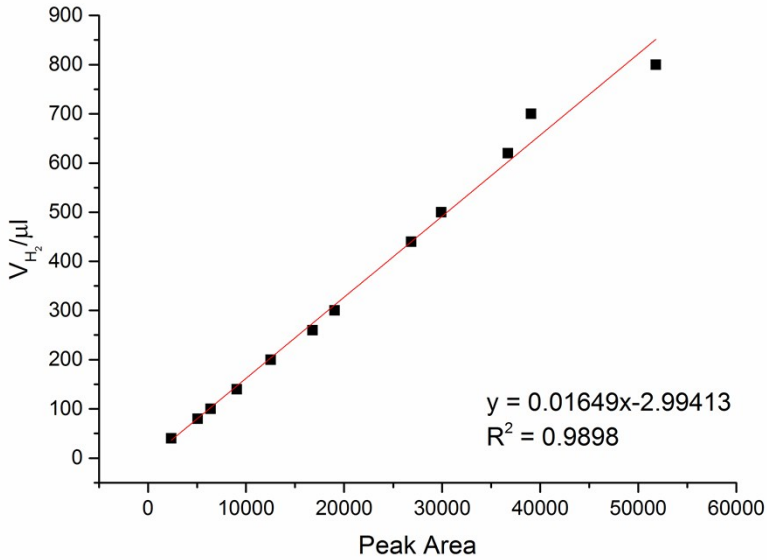

Figure S7: Calibration line used for CPC experiments. The observed peak areas of the GC are plotted against the actual injected volume of H_2 in the sample with an R^2 value of 0.9898.

For the complex **(1)** a total of 92 µl H_2 was produced in 1 h with 74% faradaic yield in MeCN. For the complex **(2)** a total of 106 µl H_2 was produced in 1 h with 73% faradaic yield. Calculations are based on the calibration line obtained by the external reference method by injection of known amounts of H_2 into the system (Fig.S7). During the CPC experiment dihydrogen is only produced from the local concentration of catalyst at the electrode surface and in these measurements a 3 mm diameter glassy carbon electrode was used.

After 1 h the area of the H_2 peak in GC is 5729 for the complex **(1)** and 6641 for the complex **(2)** according to the equation from calibration line (Fig.S7):

Complex **(1)**

$y = (0.01649x5729) - 2.99413 = 92$ µl H_2

$(92x10^{-6}) \div (24.465) = 3.76x10^{-6}$ mol H_2

Complex **(2)**

$y = (0.01649x6641) - 2.99413 = 106$ µl H_2

$(106x10^{-6}) \div (24.465) = 4.33x10^{-6}$ mol H_2

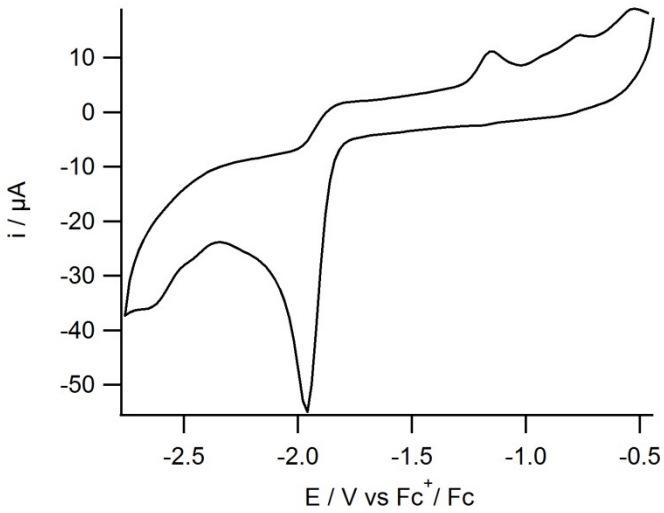

Figure S8: Cyclic voltammogram of [Ni(xbSmS)] (1mM) in an MeCN solution containing $TBAPF_6$ (0.1 M) as the supporting electrolyte and using a glassy carbon electrode at 200 mV s^{-1}.

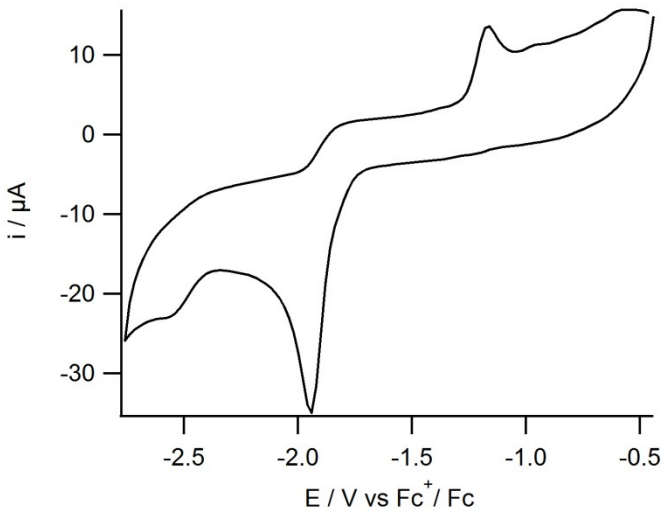

Figure S9: Cyclic voltammogram of [Ni(xbSmSe)] (1mM) in an MeCN solution containing $TBAPF_6$ (0.1 M) as the supporting electrolyte and using a glassy carbon electrode at 200 mV s^{-1}.

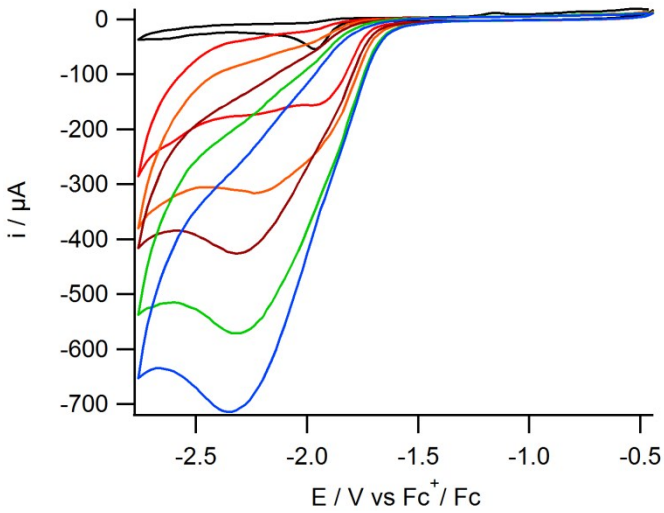

Figure S10: Cyclic voltammogram of [Ni(xbSmS)] (1mM) in an MeCN solution of $TBAPF_6$ (0.1 M) using a glassy carbon electrode at 200 mV s^{-1} in the presence of 0 (black), 10 (red), 20 (orange), 30 (brown), 40 (green), 50 (blue) mM of acetic acid.

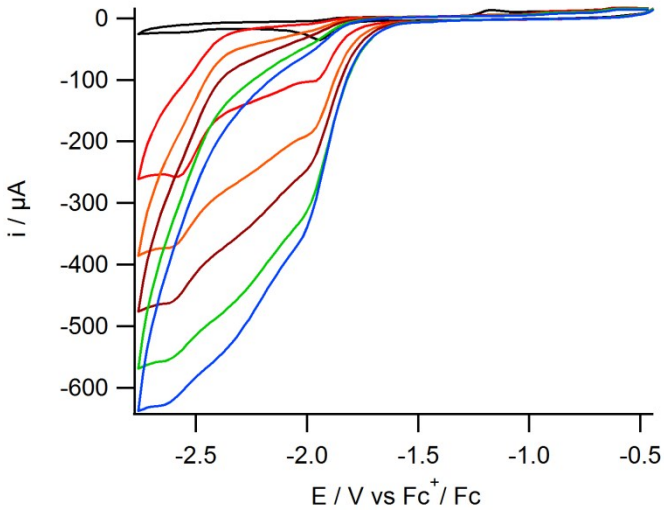

Figure S11: Cyclic voltammogram of [Ni(xbSmSe)] (1mM) in an MeCN solution of $TBAPF_6$ (0.1 M) using a glassy carbon electrode at 200 mV s^{-1} in the presence of 0 (black), 10 (red), 20 (orange), 30 (brown), 40 (green), 50 (blue) mM of acetic acid.

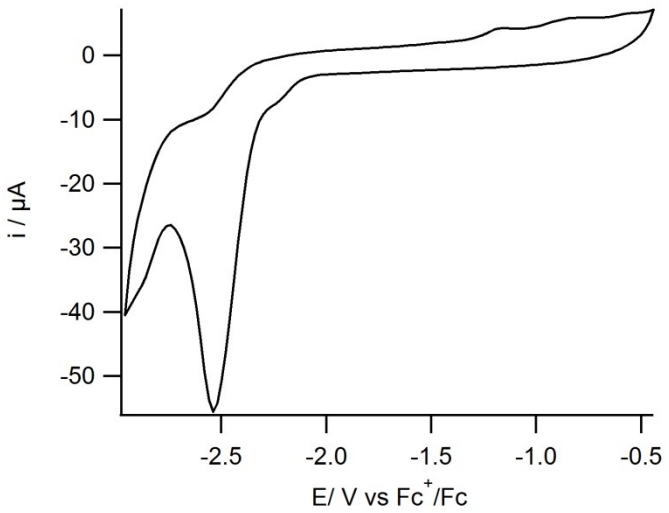

Figure S12: Cyclic voltammogram of **[**$RuCp(PPh_3)(MeCN)_2]PF_6$ (1mM) in an MeCN solution containing $TBAPF_6$ (0.1 M) as the supporting electrolyte and using a glassy carbon electrode at 200 mV s^{-1}.

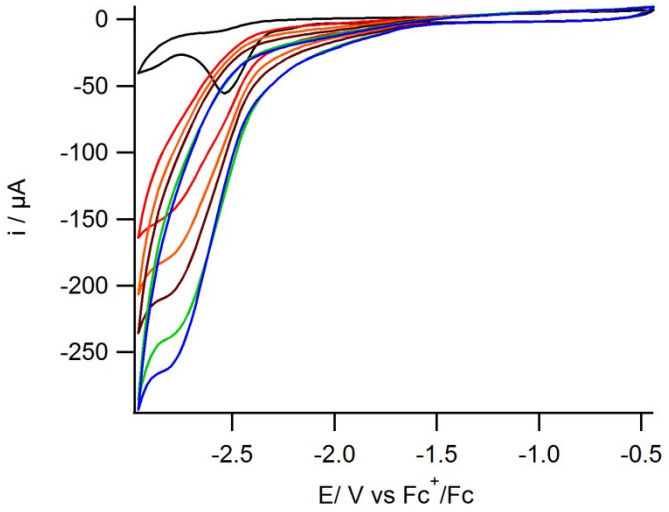

Figure S13: Cyclic voltammogram of **[**$RuCp(PPh_3)(MeCN)_2]PF_6$ (1mM) in an MeCN solution of $TBAPF_6$ (0.1 M) using a glassy carbon electrode at 200 mV s^{-1} in the presence of 0 (black), 10 (red), 20 (orange), 30 (brown), 40 (green), 50 (blue) mM of acetic acid.

References

1. R.C. Clark and J.S. Reid, *Acta Cryst.*, 1995, **A51**, 887.

2. G. M. Sheldrick, *Acta Cryst.,* 2015, **C71**, 3.