

Electronic supplementary information (ESI)

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1. Synthesis of ligands, Pt(II)-complex and **4a–5b**

1.1. PNP-C2-H (C₃₂H₃₇NO₄P₂)

Di-(2-methoxyphenyl)phosphine (115.2 mg, 0.466 mmol) is dissolved in 20 mL DMSO with 2–3 g of molecular sieve (4 Å). To activate the phosphine the base CsOH·H₂O (237.6 mg, 1.40 mmol) is added, resulting in a colour change from colourless to dark red. A second solution of 20 mL DMSO is prepared with 2–3 g of molecular sieve. *N,N*-Bis-(2-chloroethyl)amine stabilised with hydrochloric acid (41.6 mg, 0.233 mmol) is added and neutralised with a stoichiometric amount of CsOH·H₂O. This mixture is filtrated to remove the molecular sieve and added to the activated phosphine by a dropping funnel within 1.5–2 h. Then the combined solution is stirred at ambient temperature for 17 h. The resulting yellow mixture is distilled to remove DMSO. With 30 mL of 1,2-dichloroethane the crude product is dissolved and filtrated to remove the molecular sieve. The solvent is removed and the residue dissolved in 25 mL of toluene. The organic phase is extracted three times with 20 mL of deionised water and concentrated to obtain a dark yellow oil (113.0 mg, 0.201 mmol, yield: 86%).

³¹P{¹H}-NMR (121.497 MHz, CD₂Cl₂): δ (ppm) = -39.617 (s, 2P). ¹H-NMR (300.13 MHz, CD₂Cl₂): δ (ppm) = 7.343 (m, 4H, H^{Ar}), 7.138 (m, 4H, H^{Ar}), 6.901 (m, 8H, H^{Ar}), 3.755 (s, 12H, H^{MeO}), 2.746 (dd, ²J_{P-H} = 8.103 Hz, 4H, PCH₂), 2.259 (pseudo t, ³J_{H-H} = 7.203 Hz, 4H, NCH₂). Note that the proton of the secondary amine is not visible in the NMR spectra. This is due to the rapid exchange of hydrogen and deuterium atoms. ¹³C-NMR (75.476 MHz, CD₂Cl₂): δ (ppm) = 161.828 (s, 4C, C^{Ar}), 133.156 (d, 4C, C^{Ar}), 130.401 (s, 4C, C^{Ar}), 126.111 (s, 4C, C^{Ar}), 121.377 (s, 4C, C^{Ar}), 110.899 (s, 4C, C^{Ar}), 56.025 (s, 4C, MeO), 47.252 (s, 2C, PCH₂), 30.259 (s, 2C, NCH₂). **PNP-C2-H**: calc. for C₃₂H₃₇NO₄P₂ (561.60): C, 68.44; H, 6.64; N, 2.49. Found: C, 68.41; H, 6.67; N, 2.47%. No suitable mass spectrum could be obtained, possibly due to the oily nature of PNP-C2-H.

1.2. PNP-C2-Me (C₃₃H₃₉NO₄P₂)

As published elsewhere:

W. Viertl, J. Pann, R. Pehn, H. Roithmeyer, M. Bendig, A. Rodríguez-Villalón, R. Bereiter, M. Heiderscheid, T. Müller, X. Zhao, T. S. Hofer, M. E. Thompson, S. Shi and P. Brueggeller, *Faraday Discussions*, 2019, **215**, 141.

1.3. [PtCl(PNP-C2-Me)](PF₆)

[PtCl₂(COD)] (47.19 mg, 0.126 mmol) is dissolved in 20 mL dichloromethane and PNP-C2-Me (72.53 mg, 0.126 mmol) and TlPF₆ (44.15 mg, 0.126 mmol) are added. After stirring for 12 hours the solution is filtrated, concentrated and precipitated with hexane. The white powder can be crystallised with 1,2-dichlorethane/(hexane:pentane) (1:1). The product are colourless crystals. (106.67 mg, 0.112 mmol, Yield: 88.9%).

Melting point: 154 °C.

³¹P{¹H}-NMR (121.497 MHz, CH₂Cl₂): δ (ppm) = 31.033 (s, 2P, ¹J_{PtP} = 2757 Hz). **¹H-NMR** (300.13 MHz, CD₃CN): δ (ppm) = 7.797 (m, 4H, H^{Ar}), 7.628 (m, 4H, H^{Ar}), 7.511 (m, 4H, H^{Ar}), 7.004 (m, 4H, H^{Ar}), 3.932, 3.907 (2s, 12H, H^{MeO}), 3.046 (m, 4H, PCH₂), 3.003 (s, 3H, CH₃), 2.185 (dt, ³J_{H-H} = 7.803 Hz, 4H, NCH₂). **¹³C-NMR** (75.476 MHz, CD₃CN): δ (ppm) = 161.288 (s, 4C, C^{Ar}), 136.908 (s, 4C, C^{Ar}), 134.778 (s, 4C, C^{Ar}), 121.542 (s, 4C, C^{Ar}), 112.542 (s, 4C, C^{Ar}), 101.175 (s, 4C, C^{Ar}), 56.454 (s, 4C, MeO), 54.024 (s, 2C, PCH₂), 48.701 (s, 1C, CH₃), 31.443 (s, 2C, NCH₂).

Mass spectroscopy (MALDI TOF-TOF): m/z = 806.29 [M-PF₆]⁺ (calculated 806.16).

[PtCl(PNP-C2-Me)](PF₆): calc. for C₃₃H₃₉ClF₆NO₄P₃Pt (951.12): C, 41.67; H, 4.13; N, 1.47. Found: C, 41.65; H, 4.16; N, 1.44%.

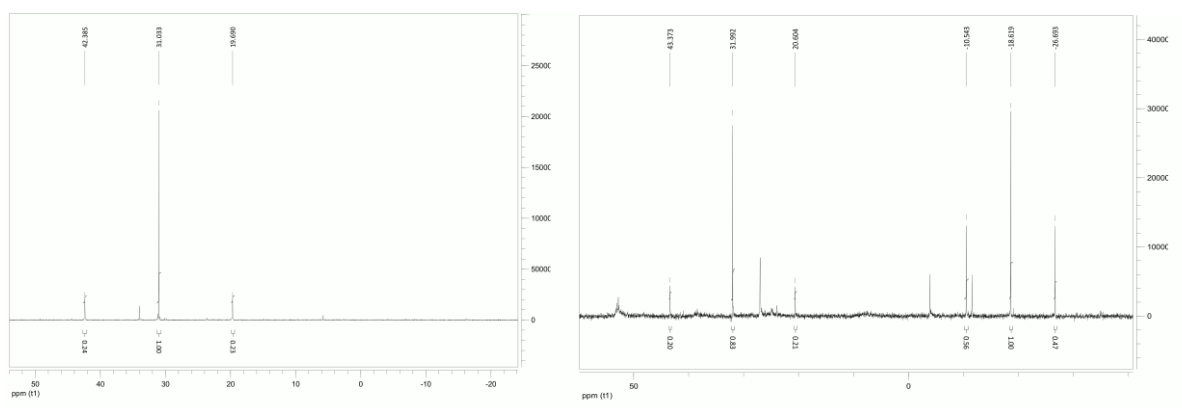


Chart 1: ³¹P{¹H} NMR spectra of [PtCl(PNP-C2-Me)](PF₆) in CH₂Cl₂ before (left) and after protonation with HCl (right) at ambient temperature.

1.4. [PdCl(PNP-C2-Me)](PF₆) **4a**

As published elsewhere:

W. Viertl, J. Pann, R. Pehn, H. Roithmeyer, M. Bendig, A. Rodríguez-Villalón, R. Bereiter, M. Heiderscheid, T. Müller, X. Zhao, T. S. Hofer, M. E. Thompson, S. Shi and P. Brueggeller, *Faraday Discussions*, 2019, **215**, 141.

1.5. [NiCl(PNP-C2-Me)](PF₆) **5a**

[NiCl₂·6H₂O] (26.32 mg, 0.1107 mmol) is dissolved in 20 mL dichloromethane and PNP-C2-Me (63.72 mg, 0.1107 mmol) and Ti(PF₆) (38.69 mg, 0.1107 mmol) are added. After stirring for 12 hours the solution is filtrated, concentrated and precipitated with diethyl ether. The red powder can be crystallised with dichloromethane/hexane (1:1). The product are red crystals. (85.56 mg, 0.1047 mmol, Yield: 94.6%).

Melting point: 108 °C.

³¹P{¹H}-NMR (121.497 MHz, CD₂Cl₂): δ (ppm) = 23.857 (s, 2P). ¹H-NMR (300.13 MHz, CD₂Cl₂): δ (ppm) = 7.939 (m, 2H, H^{Ar}), 7.807 (m, 2H, H^{Ar}), 7.662 (m, 4H, H^{Ar}), 7.182 (m, 4H, H^{Ar}), 7.075 (m, 4H, H^{Ar}), 4.038 (s, 12H, H^{MeO}), 3.076 (m, 4H, PCH₂), 2.750 (s, 3H, CH₃), 2.827 (m, 4H, NCH₂). ¹³C-NMR (75.476 MHz, CD₂Cl₂): δ (ppm) = 160.942 (s, 4C, C^{Ar}), 137.302 (s, 4C, C^{Ar}), 135.056 (s, 4C, C^{Ar}), 121.767 (s, 4C, C^{Ar}), 114.253 (s, 4C, C^{Ar}), 111.990 (s, 4C, C^{Ar}), 64.269 (s, 2C, PCH₂), 56.637 (s, 4C, MeO), 44.865 (s, 2C, NCH₂), 28.424 (s, 1C, CH₃).

Mass spectroscopy (ESI): m/z = 668.44 [M-H-PF₆]⁺ (calculated 668.76).

[NiCl(PNP-C2-Me)](PF₆), 5a: calc. for C₃₃H₃₉ClF₆NO₄P₃Ni (814.73): C, 48.65; H, 4.83; N, 1.72. Found: C, 48.65; H, 4.86; N, 1.70%.

1.6. [PdCl(PNP-C2-H)](PF₆) **4b**

[PdCl₂(COD)] (14.27 mg, 0.0500 mmol) is dissolved in 10 mL acetonitrile and PNP-C2-H (28.08 mg, 0.0500 mmol) and Ti(PF₆) (17.47 mg, 0.0500 mmol) are added. After stirring for 12 hours the solution is filtrated, concentrated and precipitated with diethyl ether. The yellow powder can be crystallised with 1,2-dichloroethane/(hexane:pentane) (1:1). The product are yellow crystals. (36.06 mg, 0.0425 mmol, Yield: 85.0%).

Melting point: 135 °C.

³¹P{¹H}-NMR (121.497 MHz, CD₂Cl₂): δ (ppm) = 36.057 (s, 2P). ¹H-NMR (300.13 MHz, CD₂Cl₂): δ (ppm) = 7.811 (m, 2H, H^{Ar}), 7.592 (m, 6H, H^{Ar}), 7.082 (m, 8H, H^{Ar}), 3.952, 3.891 (2s, 6H+6H, H^{MeO}), 3.724, 3.670 (2dt, ²J_{P-H} = 6.903 Hz, ³J_{H-H} = 4.802 Hz, 4H, PCH₂), 2.952 (m, 4H, NCH₂). Note that the proton of the secondary amine is not visible in the NMR spectra. This is due to the rapid exchange of hydrogen and deuterium atoms. ¹³C-NMR (75.476 MHz, CD₂Cl₂): δ (ppm) = 161.306 (s, 4C, C^{Ar}), 138.040 (s, 4C, C^{Ar}), 136.084 (s, 4C, C^{Ar}), 134.609 (s, 4C, C^{Ar}), 121.383 (s, 4C, C^{Ar}), 111.946 (s, 4C, C^{Ar}), 56.560 (s, 4C, C^{MeO}), 55.990 (s, 2C, C^{PCH2}), 31.962 (s, 2C, C^{NCH2}).

Mass spectroscopy (ESI): m/z = 702.44 [M-H-PF₆]⁺ (calculated 702.46).

[PdCl(PNP-C2-H)](PF₆), 4b: calc. for C₃₂H₃₇ClF₆NO₄P₃Pd (848.43): C, 45.30; H, 4.40; N, 1.65. Found: C, 45.27; H, 4.43; N, 1.67%.

X-ray structure was measured with yellow single crystals. They had been obtained from dichloromethane and hexane (*vide infra*).

1.7. [NiCl(PNP-C2-H)](PF₆) **5b**

[NiCl₂·6H₂O] (11.89 mg, 0.0500 mmol) is dissolved in 10 mL acetonitrile and PNP-C2-H (28.08 mg, 0.0500 mmol) and Na(PF₆) (17.47 mg, 0.0500 mmol) are added. After stirring for 12 hours the solution is filtrated, concentrated and precipitated with diethyl ether. The red powder can be crystallised with dichloromethane/hexane (1:1). The product are red crystals. (34.55 mg, 0.0431 mmol, Yield: 86.2%).

Melting point: 119 °C.

³¹P{¹H}-NMR (121.497 MHz, CD₂Cl₂): δ (ppm) = 25.204 (s, 2P). ¹H-NMR (300.13 MHz, CD₂Cl₂): δ (ppm) = 7.982 (m, 2H, H^{Ar}), 7.651 (m, 6H, H^{Ar}), 7.048 (m, 8H, H^{Ar}), 4.036, 4.003 (2s, 6H+6H, H^{MeO}), 3.096 (t, ³J_{H-H} = 20.709 Hz, 4H, PCH₂), 2.631 (bs, 4H, NCH₂). Note that the proton of the secondary amine is not visible in the NMR spectra. This is due to the rapid exchange of hydrogen and deuterium atoms. ¹³C-NMR (75.476 MHz, CD₂Cl₂): δ (ppm) = 161.106 (s, 4C, C^{Ar}), 137.855 (s, 4C, C^{Ar}), 136.255 (s, 4C, C^{Ar}), 134.537 (s, 4C, C^{Ar}), 121.377 (s, 4C, C^{Ar}), 111.886 (s, 4C, C^{Ar}), 56.686 (s, 4C, C^{MeO}), 56.499 (s, 2C, C^{PCH₂}), 29.716 (s, 2C, C^{NCH₂}).

Mass spectroscopy (ESI): m/z = 654.52 [M-H-PF₆]⁺ (calculated 654.73).

[NiCl(PNP-C2-H)](PF₆), **5b:** calc. for C₃₂H₃₇ClF₆NO₄P₃Ni (800.70): C, 48.00; H, 4.66; N, 1.75. Found: C, 47.97; H, 4.70; N, 1.73%.

2. Molecule structure of **4b**

The most important crystal data and bond lengths plus angles are listed in following tables. For clarity **4b** is then graphically presented in a certain pattern. Firstly, there is a representation with labels of the important atoms within the structure. Afterwards there is a figure row of a front, side and top view (Figure 1). To present the structures in an easy comprehensible manner, counter ions and solvent molecules are not displayed. Only relevant protons are shown. So, the data in the tables and the presentations of the structures by figures are assumed to be adequate to extract the striking properties of this single structure on the reader's own. Mentionable is that the structure of **4b** is not only important concerning connectivity and geometry, but was also used for DFT calculations. Therefore, it was very important to reach an R-value below 0.05. This was only possible by partial replacement of chloride *versus* bromide. Crystals of pure **4b** were not suitable for an excellent X-ray structure analysis. The ligand PNP-C2-H unequivocally coordinates in a tridentate, pincer-type fashion. The coordination geometry regarding Pd1 is square-planar, where the ethylene bridges are displaced out of this plane. Interestingly, the NH-group responsible for the initial proton transfer is located within the square plane. Furthermore, two methoxy groups shield the Pd1 centre, where the intramolecular contact distances of O1 and O2 are 3.18(1) and 3.26(2) Å, respectively (see Figure 1, top).

Crystallographic data and refinement results are given in the Supporting Information. CCDC-2282395 (for **4b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.1. [Pd(II)Cl(PNP-C2-H)](PF₆), **4b**

Table 1: Crystal data of [Pd(II)Cl(PNP-C2-H)](PF₆), **4b**

Formula	C₃₂H₃₇Br_{0.44}Cl_{0.56}F₆NO₄P₃Pd ·0.83(CH₂Cl₂)·1.89(O)	Name	4b
Mol. mass	968.49	Volume	3961.14(11) Å ³
Temperature	173(2) K	Z	4
Wavelength	0.71073 Å (Mo-K _{α1})	Diffractometer	Bruker D8 Quest Photon 100
Crystal system	Monoclinic	Calc. density	1.624 g/cm ³
Space group	P2(1)/n	Crystal size /mm	0.15·0.16·0.18
Unit cell	a=12.4218 (2) Å	Crystal colour	yellow
	b=24.4829 (4) Å	F(000)	1951.3
	c=14.1789 (2) Å	GooF on F_i²	1.112
	β=113.2767 (4)°	2θ range, deg	4.87–50.50°
Absorption coefficient, cm⁻¹	0.714	Absorption correction	multi-scan (SADABS)
Largest diff. peak and hole, e Å⁻³	0.581/-0.865	Range in hkl	-14 ≤ h ≤ 14, -29 ≤ k ≤ 29, -17 ≤ l ≤ 17
Total no. of reflections	7165	Reflections with I ≥ 2σ(I)	6673
Unique reflections	6673	Data / parameters	7010/496
Final R indices [I ≥ 2σ(I)]	R ₁ = 0.0368	Final R indices (all data)	R1 = 0.0388
	wR ₂ = 0.0808		wR ₂ = 0.0818

Table 2: Distances and angles of $[Pd(II)Cl(PNP-C2-H)](PF_6)$, **4b**

Distance between	Distance /Å	Angle between	Angle /°
Pd1 P1	2.3005 (8)	P1 Pd1 N1	84.47 (8)
Pd1 P2	2.3122 (8)	P2 Pd1 N1	85.06 (8)
Pd1 N1	2.070 (3)	P1 Pd1 Cl1	94.15 (3)
Pd1 Cl1	2.3661 (6)	P2 Pd1 Cl1	96.32 (3)
Pd1 O1	3.18 (1)	P1 Pd1 P2	169.52 (3)
Pd1 O2	3.26 (2)	N1 Pd1 Cl1	178.58 (8)
N1 H	0.81 (4)		

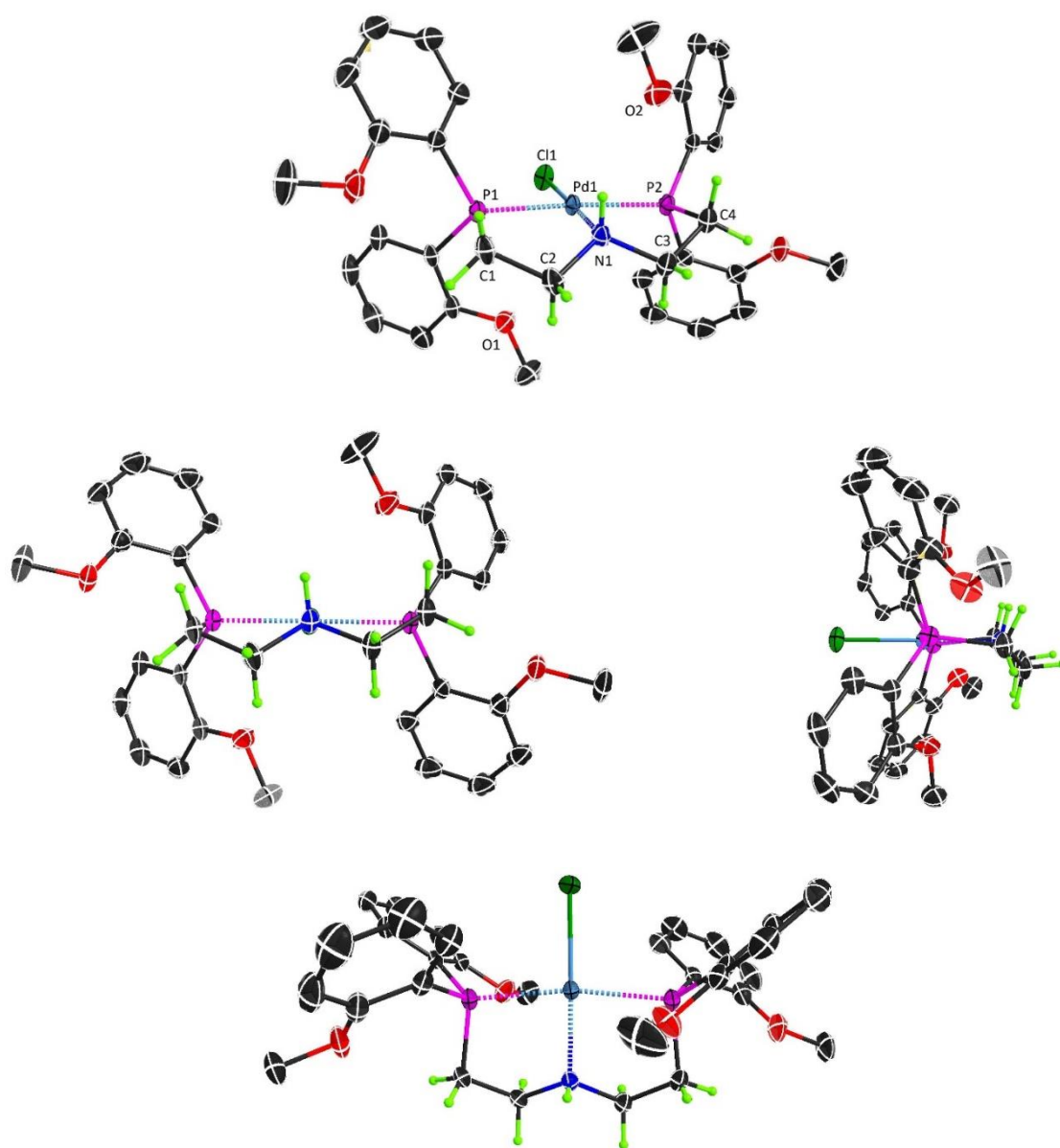


Figure 1: Molecular structure of $[Pd(II)Cl(PNP-C2-H)](PF_6)$, **4b**

3. Catalytic cycles and energy diagrams

3.1. Catalysis of $[\text{Ni}(\text{II})(\text{Cl})(\text{PNP-C2-Me})]^{2+}$ **5a**

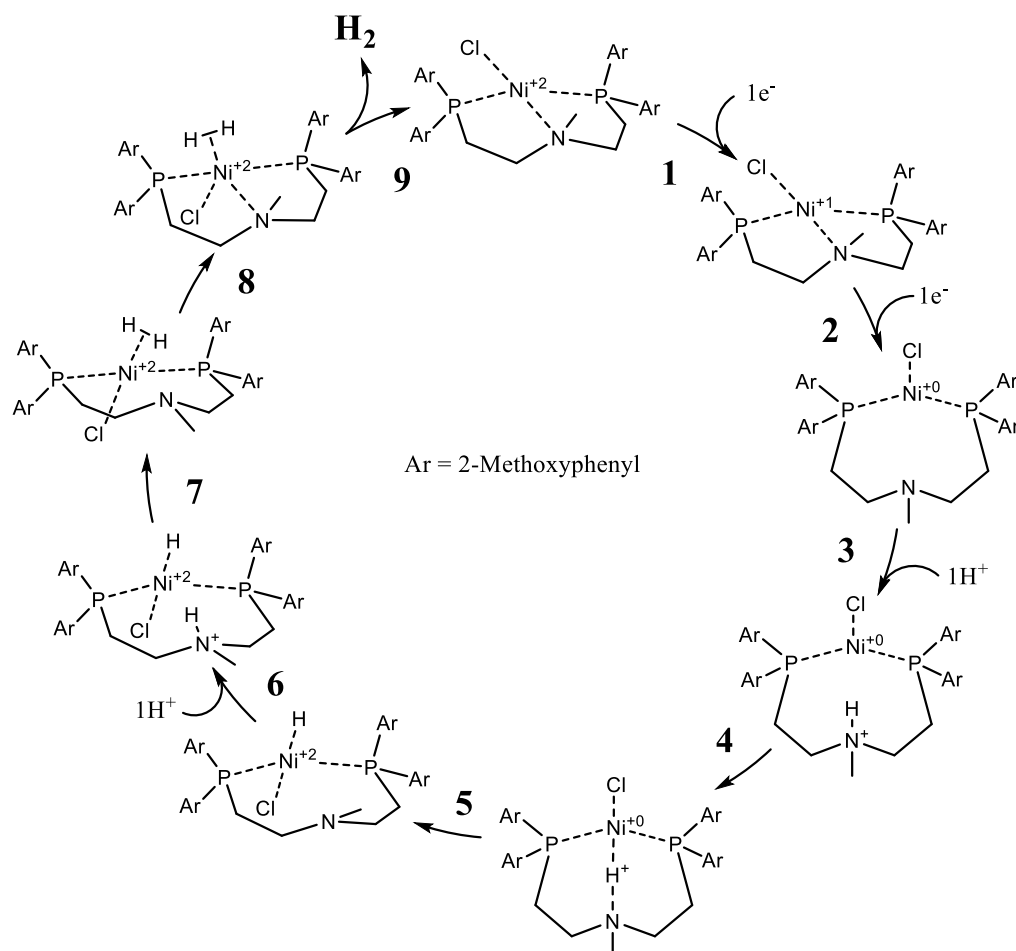


Figure 2: Catalytic cycle of $[\text{Ni}(\text{II})\text{Cl}(\text{PNP-C2-Me})]^+$ (same in gas phase as for PCM)

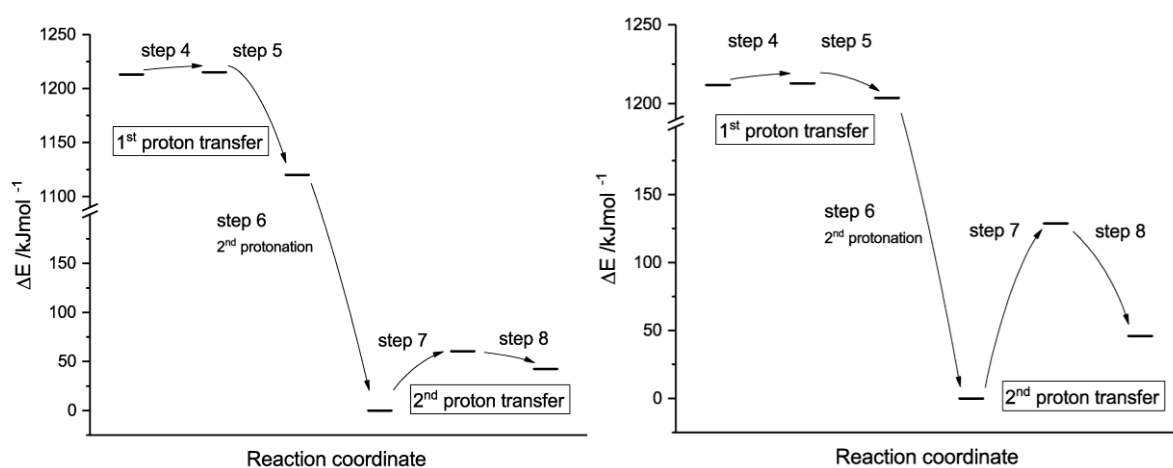


Figure 3: Energy levels of $[Ni(II)Cl(PNP-C2-Me)]^+$ (in gas phase left and as PCM right)

Table 3: Energies of proton transfers of $[Ni(II)Cl(PNP-C2-Me)]^+$ in $kJ \cdot mol^{-1}$ (in gas phase and as PCM)

Compound	$\Delta H(PT1)$	$E_a(PT1)$	$\Delta H(PT2)$	$E_a(PT2)$
Gas phase	-93.1	2.2	42.4	60.5
PCM	-8.1	1.0	46.0	128.9

3.2. Catalysis of $[\text{Ni}(\text{II})\text{Cl}(\text{PNP-C2-H})]^+ \mathbf{5b}$

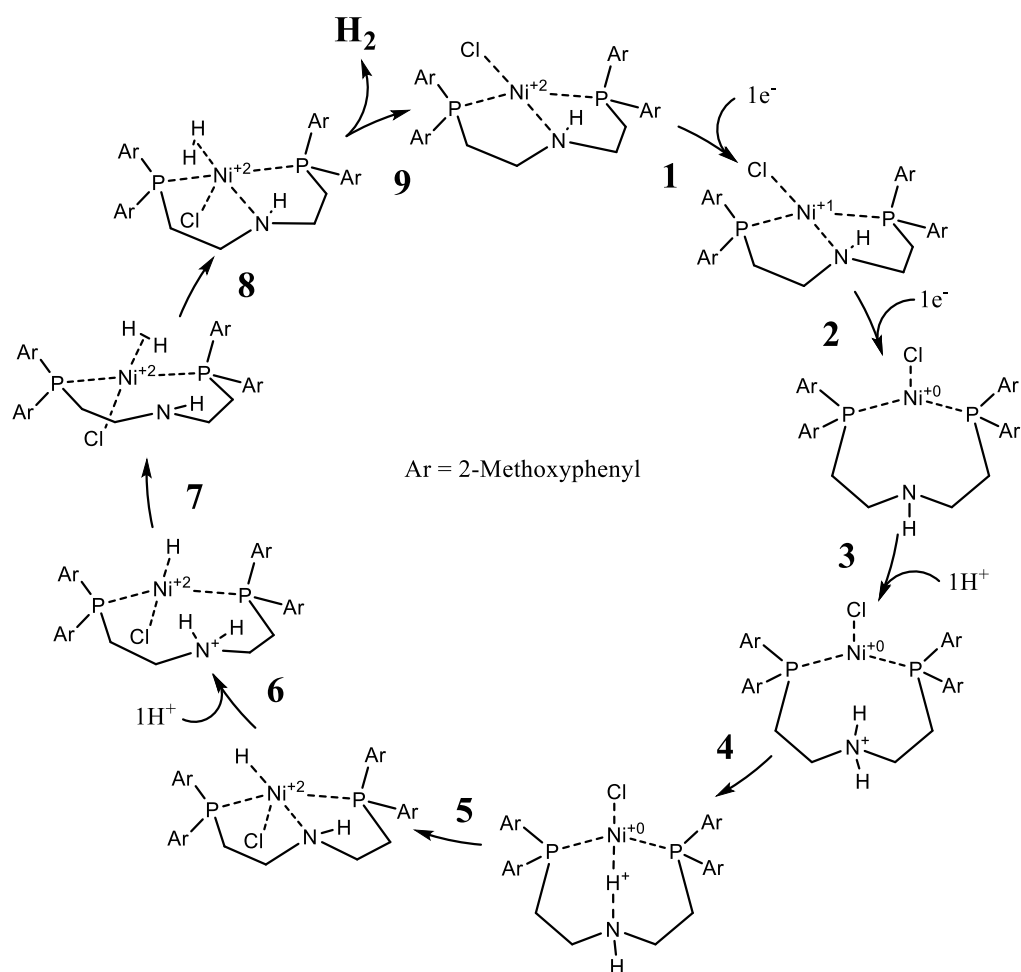


Figure 4: Catalytic cycle of $[\text{Ni}(\text{II})\text{Cl}(\text{PNP-C2-H})]^+$ (PCM)

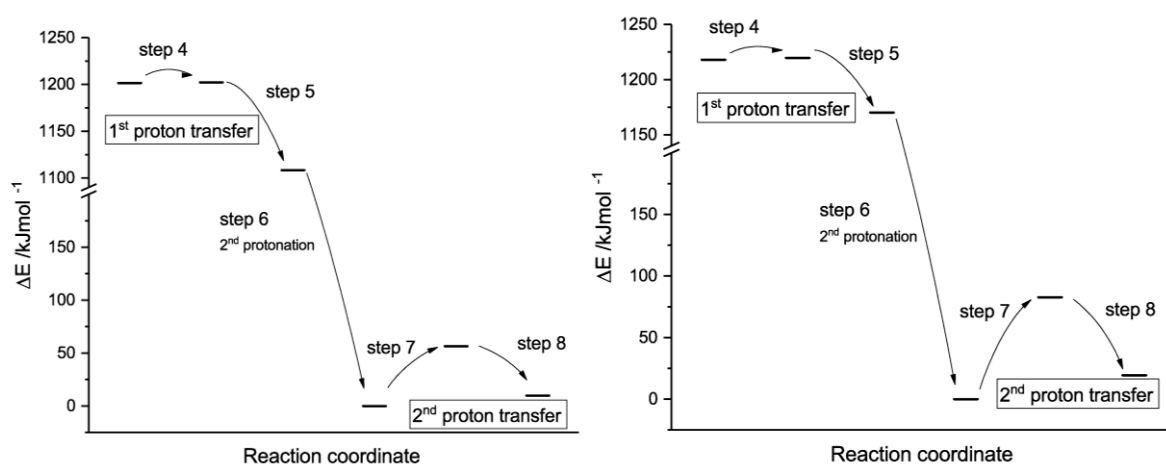


Figure 5: Energy levels of $[Ni(II)Cl(PNP-C2-H)]^+$ (in gas phase left and as PCM right)

Table 4: Energies of proton transfers of $[Ni(II)Cl(PNP-C2-H)]^+$ in $kJ \cdot mol^{-1}$ (in gas phase and as PCM)

Compound	$\Delta H(PT1)$	$E_a(PT1)$	$\Delta H(PT2)$	$E_a(PT2)$
Gas phase	-93.0	0.9	9.8	56.6
PCM	-47.8	0.2	19.4	82.8

3.3. Reaction pathways of reduction steps versus first protonation

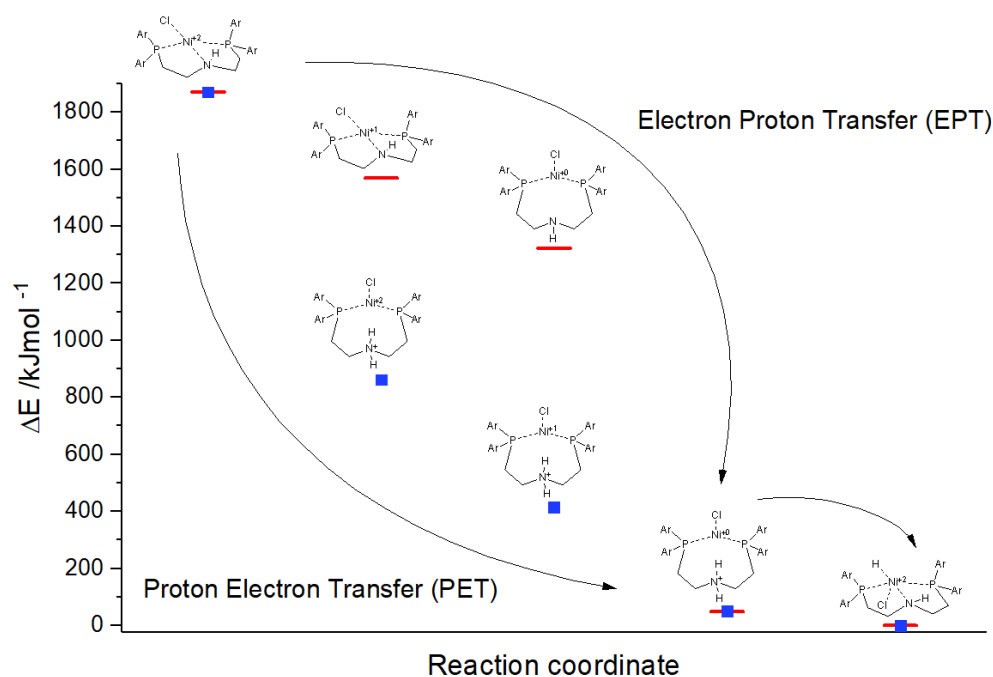


Figure 6: Two different pathways to the hydride formation, electron transfer before protonation (red bars), protonation before electron transfer (blue squares)

4. Hydrogen measurements and outcomes

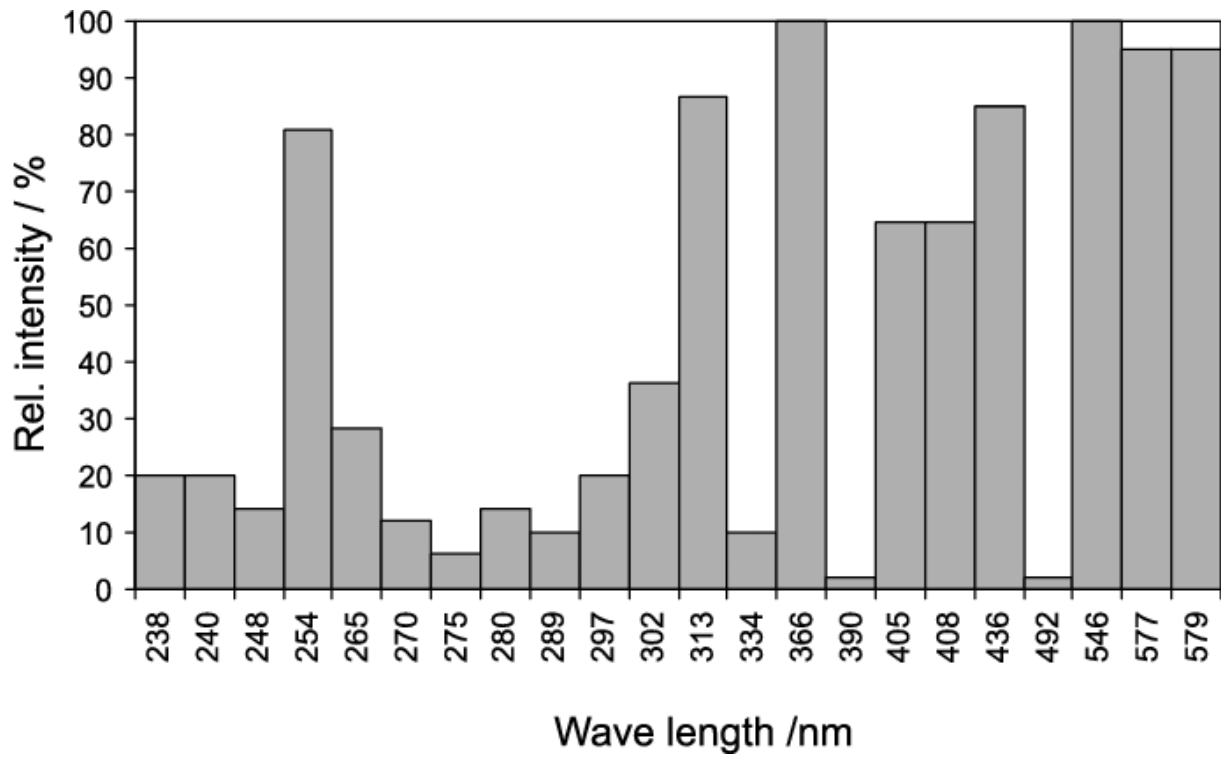


Chart 2: Spectrum of a Heraeus TQ 150 mercury lamp.

Table 5: Time-dependent hydrogen production of water reduction catalyst (WRC) **4a** Pd(PNP-C2-Me), addition of extra equivalent of photosensitiser (PS) after each hydrogen measurement except for experiments with 25-fold excess of PS from the beginning, irradiation with 470 nm and 100 mW, measurement of hydrogen concentration with a maximal relative standard deviation of 1.5 %. Comparison of compounds **4a** with starting PS/WRC ratio of 1, 2, 5 and 25.

t /min	TON(WRC) /-	n(WRC) /mol	n(PS) /mol	ratio PS/WRC
results for Pd pincer complexes with tertiary amine				
4a Pd(PNP-C2-Me) + PS				
0,0	0,0	1,30E-06	1,30E-06	1
15,0	26,4		1,30E-06	1
30,0	32,4		1,30E-06	1
45,0	33,2		2,58E-06	2
60,0	137,4		5,15E-06	4
75,0	300,6		5,15E-06	4
90,0	315,2		5,15E-06	4
4a Pd(PNP-C2-Me) + 2PS				
0,0	0,0	1,34E-06	2,69E-06	2
20,0	73,9		5,38E-06	4
40,0	303,1		8,07E-06	6
60,0	431,1		1,08E-05	8
80,0	538,7		1,35E-05	10
100,0	660,8		1,59E-05	12
120,0	767,8		1,88E-05	14
140,0	887,7		1,88E-05	14
4a Pd(PNP-C2-Me) + 5PS				
0,0	0,0	1,02E-06	5,10E-06	5
30,0	202,3		1,02E-05	10
60,0	337,8		1,53E-05	15
90,0	540,9		2,04E-05	20
120,0	722,3		2,55E-05	25
150,0	971,9		2,55E-05	25
4a Pd(PNP-C2-Me) + 25PS				
0,0	0,0	9,86E-07	2,45E-05	25
30,0	30,2		2,45E-05	25
45,0	69,3		2,45E-05	25
55,0	110,3		2,45E-05	25

Table 6: Time-dependent hydrogen production of water reduction catalyst (WRC) **4b** Pd(PNP-C2-H), addition of extra equivalent of photosensitiser (PS) after each hydrogen measurement except for experiments with 25-fold excess of PS from the beginning, irradiation with 470 nm and 100 mW, measurement of hydrogen concentration with a maximal relative standard deviation of 1.5 %. Comparison of compounds **4b** with starting PS/WRC ratio of 1, 2, 5 and 25.

	TON(WRC) /-	n(WRC) /mol	n(PS) /mol	ratio PS/WRC
results for Pd pincer complexes with secondary amine				
	4b Pd(PNP-C2-H) + PS			
0,0	0,0	1,28E-06	1,28E-06	1
15,0	60,0		1,28E-06	1
30,0	61,3		1,28E-06	1
45,0	78,4		2,56E-06	2
60,0	284,6		5,13E-06	4
75,0	504,3		5,13E-06	4
90,0	539,9		5,13E-06	4
	4b Pd(PNP-C2-H) + 2PS			
0,0	0,0	1,03E-06	2,05E-06	2
20,0	91,4		4,10E-06	4
40,0	338,6		6,15E-06	6
60,0	496,1		8,20E-06	8
80,0	645,7		1,03E-05	10
100,0	822,3		1,21E-05	12
120,0	1017,6		1,47E-05	14
140,0	1306,4		1,47E-05	14
	4b Pd(PNP-C2-H) + 5PS			
0,0	0,0	1,41E-06	7,07E-06	5
30,0	475,3		1,41E-05	10
60,0	761,3		2,12E-05	15
90,0	1235,1		2,83E-05	20
120,0	1781,3		3,54E-05	25
150,0	2236,9		3,54E-05	25
	4b Pd(PNP-C2-H) + 25PS			
0,0	0,0	9,86E-07	2,45E-05	25
30,0	476,0		2,45E-05	25
45,0	521,0		2,45E-05	25
55,0	513,6		2,45E-05	25

Table 7: Time-dependent hydrogen production of water reduction catalysts (WRC) **4a** Pd(PNP-C2-Me), **4b** Pd(PNP-C2-H), **5a** Ni(PNP-C2-Me) and **5b** Ni(PNP-C2-H), addition of extra equivalent of photosensitiser (PS) after each hydrogen measurement, irradiation with 470 nm and 100 mW (except for nickel catalysts – 160 mW), measurement of hydrogen concentration with a maximal relative standard deviation of 1.5 %. Comparison of compounds **4a**, **4b**, **5a** and **5b** with starting PS/WRC ratio of 5.

t /min	TON(WRC) /-	n(WRC) /mol	n(PS) /mol	ratio PS/WRC
	4b Pd(PNP-C2-H) + 5PS			
0,0	0,0	1,41E-06	7,07E-06	5
30,0	475,3		1,41E-05	10
60,0	761,3		2,12E-05	15
90,0	1235,1		2,83E-05	20
120,0	1781,3		3,54E-05	25
150,0	2236,9		3,54E-05	25
	4a Pd(PNP-C2-Me) + 5PS			
0,0	0,0	1,02E-06	5,10E-06	5
30,0	202,3		1,02E-05	10
60,0	337,8		1,53E-05	15
90,0	540,9		2,04E-05	20
120,0	722,3		2,55E-05	25
150,0	971,9		2,55E-05	25
	5b Ni(PNP-C2-H) + 5PS			
0,0	0,0	1,67E-06	8,28E-06	5
20,0	8,2		1,67E-05	10
40,0	12,8		2,52E-05	15
60,0	15,9		3,36E-05	20
80,0	19,6		4,20E-05	25
100,0	25,5		4,20E-05	25
	5a Ni(PNP-C2-Me) + 5PS			
0,0	0,0	1,62E-06	8,10E-06	5
20,0	2,3		1,62E-05	10
40,0	3,9		2,43E-05	15
60,0	4,8		3,24E-05	20
80,0	5,7		3,24E-05	20

Table 8: Time-dependent hydrogen production of water reduction catalysts (WRC) **4a** Pd(PNP-C2-Me) and **4b** Pd(PNP-C2-H) with 25-fold excess of PS from the beginning, irradiation with 470 nm and 100 mW, measurement of hydrogen concentration with a maximal relative standard deviation of 1.5 %. Comparison of compounds **4a** and **4b** in H₂O and D₂O with starting PS/WRC ratio of 25, measured with gas chromatography as well as mass spectrometry (sensitive to hydrogen isotopes)

t /min	TON(WRC) /-	n(WRC) /mol	n(PS) /mol	ratio PS/WRC
	4b Pd(PNP-C2-H) in H ₂ O			
0,0	0,0	1,46E-06	3,64E-05	25
30,0	476,0		3,64E-05	25
45,0	521,0		3,64E-05	25
55,0	513,6		3,64E-05	25
	4a Pd(PNP-C2-Me) in H ₂ O			
0,0	0,0	9,86E-07	2,45E-05	25
30,0	30,2		2,45E-05	25
45,0	69,3		2,45E-05	25
55,0	110,3		2,45E-05	25
	4b Pd(PNP-C2-H) in D ₂ O			
0,0	0,0	1,43E-06	3,58E-05	25
30,0	259,6		3,58E-05	25
45,0	426,2		3,58E-05	25
55,0	501,5		3,58E-05	25
	4a Pd(PNP-C2-Me) in D ₂ O			
0,0	0,0	1,04E-06	2,61E-05	25
30,0	22,0		2,61E-05	25