# Bimetallic Nickel–Cobalt Hydride in H<sub>2</sub> Activation and Catalytic Proton Reduction

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#### 1. General information

All reactions were carried out under dry nitrogen atmosphere using standard Schlenk techniques. All reagents were purchased from Sigma–Aldrich, and used as received. All solvents were stored under nitrogen. All NMR spectra were recorded in J. Young NMR tubes using Bruker Avance 500 spectrometers. <sup>31</sup>P{<sup>1</sup>H} NMR spectra were referenced to external 8% H<sub>3</sub>PO<sub>4</sub> as internal standards. Cyclic voltammetry was measured by a CHI 760e electrochemical workstation (Shanghai Chen Hua Instrument Co., Ltd.) under nitrogen at room temperature (electrode types: a glassy carbon electrode as working electrode, Pt wire electrode as counter electrode, and Ag wire electrode as reference electrode). (dppe)Ni(pdt) and [Cp\*CoCl<sub>2</sub>]<sub>2</sub>was prepared according to the reported methods.<sup>1,2</sup>

#### 2. Experimental procedures

[(dppe)Ni(pdt)(Cl)CoCp\*]<sup>+</sup>, [1Cl]<sup>+</sup>. Ni(pdt)(dppe) was added to a dark green solution of [Cp\*CoCl<sub>2</sub>]<sub>2</sub> (197 mg, 0.42 mmol) in 60 mL of CH<sub>2</sub>Cl<sub>2</sub> (473 mg, 0.84 mmol), followed by the addition of KPF<sub>6</sub> (200 mg, 1.08 mmol). After stirring for 5 h, the brown solution was collected by filtration and concentrated to 5 mL. Then 30 mL of hexane was added the concentrate to afford brown precipitate. The precipitate was washed with  $3 \times 10$  mL of hexane, and dried under vacuum. Yield: 650 mg (83 %). <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 7.51–7.86 (m, 20H, C<sub>6</sub>H<sub>5</sub>), 2.45 (m, 2H, PCH<sub>2</sub>), 2.31 (m, 3H, SCH<sub>2</sub>CH<sub>2</sub>), 2.05 (m, 2H, PCH<sub>2</sub>), 1.88 (m, 1H, SCH<sub>2</sub>CH<sub>2</sub>), 1.45 (m, 2H, SCH<sub>2</sub>). 1.31 (s, 15H, C<sub>5</sub>H<sub>15</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>CN): δ 54.4 (s). ESI-MS: calcd for [1Cl]<sup>+</sup>, 791.0812; found, 791.0796. Anal. Calcd. for C<sub>39</sub>H<sub>45</sub>P<sub>3</sub>S<sub>2</sub>F<sub>6</sub>CoNiCl: C, 49.94; H, 4.84. Found: C, 50.62; H, 4.97.

**[(dppe)Ni(pdt)CoCp\*], 1.** A mixture of [1Cl]<sup>+</sup> (243 mg, 0.26 mmol) and Cp<sub>2</sub>Co (98 mg, 0.52 mmol) was stirred in 35 mL of THF at room temperature for 15 min to obtain red brown solution. And the solvent was removed under reduced pressure. The residue was extracted by ~ 5 mL of toluene through a pad of Celite and the extract was layered with 50 mL of hexane to yield black crystals at -30 °C. Yield: 120 mg (61 %). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.33–7.88 (m, 20H, C<sub>6</sub>H<sub>5</sub>), 2.07 (m, 2H, PCH<sub>2</sub>), 1.90 (m, 4H, SCH<sub>2</sub>CH<sub>2</sub>), 1.76 (m, 2H, PCH<sub>2</sub>), 1.45 (s, 15H, C<sub>5</sub>H<sub>15</sub>) 1.31 (m, 2H, S SCH<sub>2</sub>CH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  42.7 and 42.2 (br, dppe). ESI-MS: calcd for **1**, 756.1123; found, 756.1090. Anal. Calcd. for C<sub>39</sub>H<sub>45</sub>P<sub>2</sub>S<sub>2</sub>CoNi: C, 61.84; H, 5.99. Found: C, 62.51; H, 6.23.

[(dppe)Ni(pdt)(H)CoCp\*]<sup>+</sup>, [1H]<sup>+</sup>. Method A, Complex 1 (151 mg, 0.20 mmol) was dissolved into 20 mL of THF and Cl<sub>2</sub>CHCOOH (16.5  $\mu$ L, 0.20 mmol) was added to give dark brown solution. After stirring 15 min, the solution was filtered through celite and dried under reduced pressure. And the product was washed with 3×10 mL of hexane. Single crystal was obtained by layering hexane into CH<sub>2</sub>Cl<sub>2</sub> solution at –30 °C. Yield: 150 mg (89 %). Method B, To a solution of [1Cl]<sup>+</sup> (295 mg, 0.32 mmol) in 30 mL of acetonitrile was added a solution of NaBH<sub>4</sub> (12 mg, 0.32 mmol) in 10 mL of ethanol, immediately producing a dark brown solution. The solution was filtered through Celite, and concentrated under reduced pressure. 50 mL of Et<sub>2</sub>O was added to obtain the precipitate. The solid was dried under vacuum. Yield: 220 mg (77 %). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.55–7.76 (m, 20H, C<sub>6</sub>H<sub>5</sub>), 2.54

(m, 2H, PC*H*<sub>2</sub>), 2.50 (m, 2H, PC*H*<sub>2</sub>), 2.46 (m, 2H, SC*H*<sub>2</sub>CH<sub>2</sub>), 1.83 (m, 2H, SC*H*<sub>2</sub>CH<sub>2</sub>), 1.73 (m, 2H, SCH<sub>2</sub>C*H*<sub>2</sub>), 1.49 (s, 15H, C<sub>5</sub>*H*<sub>15</sub>), -9.76 (1H, br, Co(*H*)Ni). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  67.5 (s). ESI-MS: calcd for [1H]<sup>+</sup>, 757.1202; found, 757.1175. Anal. Calcd. for C<sub>39</sub>H<sub>46</sub>P<sub>3</sub>S<sub>2</sub>F<sub>6</sub>CoNi: C, 51.85; H, 5.13. Found: C, 52.24; H, 5.30.

**Reaction of [1H]**<sup>+</sup> with D<sub>2</sub>O. A solution of [1H]<sup>+</sup> (20 mg, 0.022 mmol) in 0.5 mL of  $d_3$ -acetonitrile was prepared in a J. Young NMR tube. The sample was stored at room temperature and 10 equiv. of D<sub>2</sub>O was added. The <sup>1</sup>H NMR spectrum was recorded each 30 min and the hydride signal ( $\delta$  –9.65) diminished gradually, indicating the formation of deuterated species. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum had no obvious change. <sup>2</sup>H NMR (CH<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –9.66 (1D, br, Co(*D*)Ni), <sup>31</sup>P{<sup>1</sup>H} NMR (D<sub>2</sub>O): 67.38 (s). ESI-MS: calcd for [1D]<sup>+</sup>, 758.1264; found, 758.1216.

[(**dppe**)**Ni**(**pdt**)**CoCp\***]<sup>+</sup>, [1]<sup>+</sup>. **1** (50 mg, 0.066 mmol) was dissolved into 10 mL of acetonitrile and the solution of AgBF<sub>4</sub> (13 mg, 0.066 mmol) in 3 mL of acetonitrile was dropwise added. After 5 min, the solution was the solution was filtered through Celite and concentrated into 2 mL. The product was precipitated by the addition of 15 mL of Et<sub>2</sub>O. Yield: 45 mg (81 %). ESI-MS: calcd for [1]<sup>+</sup>, 756.1123; found, 756.1088. Anal. Calcd. for C<sub>39</sub>H<sub>45</sub>P<sub>2</sub>S<sub>2</sub>BF<sub>4</sub>CoNi: C, 55.48; H, 5.37. Found: C, 55.90; H, 5.94.

 $[(dppe)Ni(pdt)CoCp*]^{2+}$ ,  $[1]^{2+}$ . To a solution of 1 (50 mg, 0.066 mmol) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> was added AgBF<sub>4</sub> (26 mg, 0.133 mmol). After 15 min, the solvent was removed under reduced pressure and the product was washed with 3×10 mL of hexane. Yield: 53 mg (86 %). <sup>31</sup>P{<sup>1</sup>H} NMR (D<sub>2</sub>O): 59.5 (s).

[(**dppe**)Ni(**pdt**)Co(NCMe)C**p**\*]<sup>2+</sup>, [1(NCMe)]<sup>2+</sup>. Complex [1]<sup>2+</sup> (25 mg, 0.054 mmol) was dissolved into 5 mL of acetonitrile, 20 mL of Et<sub>2</sub>O was added to form a needle-like crystal. Yield: 20 mg (77 %). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.65–7.82 (m, 20H, C<sub>6</sub>H<sub>5</sub>), 3.11 (m, 2H, PCH<sub>2</sub>), 2.77 (m, 2H, PCH<sub>2</sub>), 2.66 (m, 1H, SCH<sub>2</sub>CH<sub>2</sub>), 2.58 (m, 3H, SCH<sub>2</sub>CH<sub>2</sub>), 2.35 (m, 2H, SCH<sub>2</sub>), 2.17 (s, 3H, CH<sub>3</sub>CN), 1.99 (s, 15H, C<sub>5</sub>H<sub>15</sub>) <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 54.69 and 49.97 (br, dppe). ESI-MS: calcd for ([1(NCMe)]<sup>2+</sup>–MeCN), 378.0562; found, 378.0558. Anal. Calcd. for C<sub>41</sub>H<sub>48</sub>NP<sub>2</sub>S<sub>2</sub>B<sub>2</sub>F<sub>8</sub>CoNi: C, 50.66; H, 4.98. Found: C, 51.02; H, 5.15. **H**<sub>2</sub> **splitting.** In a Schlenk flask,  $[1(NCMe)]^{2+}$  (20 mg, 0.02 mmol) was dissolved in 15 mL of MeCN, the solution changed to dark brown after bubbling hydrogen (1 atm) for 5 min. The CH<sub>3</sub>OH solution of CH<sub>3</sub>ONa (1 mg, 0.02 mmol) was then added. the solvent was removed under reduced pressure and the product was washed with 3×10 mL of Et<sub>2</sub>O. Yield: 15 mg (89 %). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 1.49 (s, 15H, C<sub>5</sub>H<sub>15</sub>), -9.77 (1H, s, Co-H). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 67.52.

**Electrochemical H<sub>2</sub> production**. A solution of  $[1H]^+$  (4.5 mg, 0.005 mmol) in 5 mL of MeCN was prepared in the CV cell, and was treated with successive equivalent of Cl<sub>2</sub>CHCOOH. For blank experiment, a solution of acid in 5 mL of MeCN was recorded with same sweep speed of 100 mV/s.

### 3. Figures



**Fig. S1** <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of [(dppe)Ni(pdt)(Cl)CoCp\*]<sup>+</sup>, [1Cl]<sup>+</sup> in CD<sub>3</sub>CN. (H<sub>3</sub>PO<sub>4</sub> as internal standard)



**Fig. S2** <sup>1</sup>H NMR spectrum of [(dppe)Ni(pdt)(Cl)CoCp\*]<sup>+</sup>, [1Cl]<sup>+</sup> in CD<sub>3</sub>CN. Resonances at 5.4 (CH<sub>2</sub>Cl<sub>2</sub>); 4.2 (H<sub>3</sub>PO<sub>4</sub>); 2.2 (H<sub>2</sub>O); 1.97 (CH<sub>3</sub>CN); 1.28, 0.89 (hexane) are from solvent.



Fig. S3 ESI-MS of [(dppe)Ni(pdt)(Cl)CoCp\*]<sup>+</sup>, [1Cl]<sup>+</sup>.

*Result:* Calcd for [1Cl]<sup>+</sup>, 791.0812; found, 791.0796.



**Fig. S4** <sup>31</sup>P NMR spectrum of [(dppe)Ni(pdt)CoCp\*], **1** in CD<sub>2</sub>Cl<sub>2</sub>. The signal of H<sub>3</sub>PO<sub>4</sub> is at 0 ppm. *Result:* The signal at 43.40 ppm is for [Ni<sup>I</sup>Co<sup>II</sup>] species and the signal at 42.35 ppm is for [Ni<sup>II</sup>Co<sup>I</sup>] species.



**Fig. S5** <sup>1</sup>H NMR spectrum of [(dppe)Ni(pdt)CoCp\*], **1** in CD<sub>2</sub>Cl<sub>2</sub>. Resonances at 5.4 (CH<sub>2</sub>Cl<sub>2</sub>); 4.7 (H<sub>2</sub>O); 3.43, 1.15 (Et<sub>2</sub>O); 1.28, 0.89 (hexane) are from solvent.



Fig. S6 ESI-MS of [(dppe)Ni(pdt)CoCp\*], 1.

*Result:* Calcd for 1, 756.1123; found, 756.1090.



Fig. S7 <sup>31</sup>P NMR spectrum of [(dppe)Ni(pdt)CoCp\*], 1 in benzonitrile at (a) 298 K and (b) 323 K.



 $\label{eq:Fig. S8} \ensuremath{^{31}P}{^{1}H} \ensuremath{\ NMR\ } spectrum \ of \ [(dppe)Ni(pdt)(H)CoCp*]^+, \ [1H]^+ \ in \ CD_2Cl_2.$ 



**Fig. S9** <sup>1</sup>H NMR spectrum of  $[(dppe)Ni(pdt)(H)CoCp^*]^+$ ,  $[1H]^+$  in CD<sub>2</sub>Cl<sub>2</sub>. Resonances at 5.4 (CH<sub>2</sub>Cl<sub>2</sub>); 1.28, 0.89 (hexane) are from solvent.



Fig. S10 ESI-MS of  $[(dppe)Ni(pdt)(H)CoCp^*]^+$ ,  $[1H]^+$ .

*Result:* Calcd for [1H]<sup>+</sup>, 757.1202; found, 757.1175.



Fig. S11  ${}^{31}P{}^{1}H$  NMR spectrum of [(dppe)Ni(pdt)(H)CoCp\*]<sup>+</sup>, [1H]<sup>+</sup> at various temperatures in CD<sub>2</sub>Cl<sub>2</sub>.



**Fig. S12** <sup>1</sup>H NMR spectrum of  $[(dppe)Ni(pdt)(H)CoCp^*]^+$ ,  $[1H]^+$  at various temperatures in  $CD_2Cl_2$ .



**Fig. S13** <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of [(dppe)Ni(pdt)(D)CoCp\*]<sup>+</sup>, [1D]<sup>+</sup> in CH<sub>2</sub>Cl<sub>2</sub>. (H<sub>3</sub>PO<sub>4</sub> as internal standard).



Fig. S14 <sup>2</sup>H NMR spectrum of  $[(dppe)Ni(pdt)(D)CoCp^*]^+$ ,  $[1D]^+$  in CH<sub>2</sub>Cl<sub>2</sub>.



**Fig. S15** ESI-MS of [(dppe)Ni(pdt)(D)CoCp\*]<sup>+</sup>, [1D]<sup>+</sup>.

*Result:* Calcd for [1D]<sup>+</sup>, 758.1264; found, 758.1216.



Fig. S16 Plot of the hydride integration vs time for the reaction of  $[1H]^+$  with excess D<sub>2</sub>O in CD<sub>3</sub>CN. *Results:*  $k = 5.023 \times 10^{-5} \text{ s}^{-1}$ ,  $t_{1/2} = 3.83 \text{ h}$ .



Fig. S17  ${}^{31}P{}^{1}H$  NMR spectrum of 1 with [Et<sub>3</sub>NH]BF<sub>4</sub> in PhCN up to the balance.

![](_page_23_Figure_0.jpeg)

Fig. S18 ESI-MS of  $[(dppe)Ni(pdt)CoCp^*]^+$ ,  $[1]^+$ .

*Result:* Calcd for [1]<sup>+</sup>, 756.1123; found, 756.1088.

![](_page_24_Figure_0.jpeg)

Fig. S19 Cyclic voltammogram of 1 recorded in PhCN with 0.1 M NBu<sub>4</sub>PF<sub>6</sub>, scan rate 100 mV/s.

![](_page_25_Figure_0.jpeg)

**Fig. S20** <sup>31</sup>P NMR spectrum of  $[(dppe)Ni(pdt)CoCp^*]^{2+}$ ,  $[1]^{2+}$  in CH<sub>2</sub>Cl<sub>2</sub>.

![](_page_26_Figure_0.jpeg)

**Fig. S21** <sup>31</sup>P NMR spectrum of  $[1]^{2+}$  (red) and  $[1(NCMe)]^{2+}$  (purple) in acetonitrile- $d_3$ . *Results:* 54.69, 49.98 ppm.

![](_page_27_Figure_0.jpeg)

**Fig. S22** <sup>1</sup>H NMR spectrum of  $[(dppe)Ni(pdt)Co(NCMe)Cp^*]^{2+}$ ,  $[1(NCMe)]^{2+}$  in acetonitrile- $d_3$ .

![](_page_28_Figure_0.jpeg)

Fig. S23 ESI-MS of  $[(dppe)Ni(pdt)Co(NCMe)Cp^*]^{2+}$ ,  $[1(NCMe)]^{2+}$ .

*Results:* Calcd for ( [1(NCMe)]<sup>2+</sup>–MeCN), 378.0562; found, 378.0558.

![](_page_29_Figure_0.jpeg)

**Fig. S24** Control experiments (top: <sup>31</sup>P NMR; bottom: <sup>1</sup>H NMR) of H<sub>2</sub> splitting. MeCN/MeOH (v:v = 1:1), (a)  $[1(NCMe)]^{2+}$ , H<sub>2</sub> and CH<sub>3</sub>ONa; (b)  $[1(NCMe)]^{2+}$  and CH<sub>3</sub>ONa; (c)  $[1(NCMe)]^{2+}$  and H<sub>2</sub>.

![](_page_30_Figure_0.jpeg)

Fig. S25 Comparison of cyclic voltammograms in  $Cl_2CHCOOH$  solution before and after the addition of  $[1H]^+$ . Conditions: 1 mM sample in CH<sub>3</sub>CN, 0.1 M *n*-NBu<sub>4</sub>PF<sub>6</sub> as the supporting electrolyte; scan rate = 100 mV/s.

Acid (µL)	$i_{\rm cat}/i_{\rm p}$	TOF $(s^{-1})$	$E_{\text{cat1/2}}(\mathbf{V})$	Overpotential (V)	
1	1.416	0.389	-1.325	0.512	
2	1.622	0.510	-1.337	0.515	
4	2.717	1.432	-1.342	0.511	
6	3.377	2.212	-1.353	0.517	
8	3.493	2.367	-1.339	0.499	
10	5.366	5.586	-1.367	0.524	
12	6.150	7.336	-1.377	0.532	
14	7.482	10.861	-1.375	0.528	
16	8.258	13.231	-1.395	0.546	
18	8.786	14.977	-1.392	0.541	
20	9.439	17.285	-1.407	0.555	
25	11.690	26.512	-1.43	0.575	
30	13.948	37.744	-1.45	0.593	
35	15.317	45.511	-1.45	0.591	
40	17.979	62.709	-1.48	0.619	
45	19.994	77.553	-1.492	0.630	
50	21.732	91.624	-1.486	0.622	
55	25.209	123.289	-1.486	0.621	
60	25.503	126.182	-1.506	0.640	
65	27.124	142.723	-1.5	0.633	
70	28.131	153.522	-1.52	0.652	
75	29.324	166.823	-1.517	0.648	
85	32.824	209.022	-1.535	0.665	
90	35.472	244.097	-1.531	0.660	

**Table S1.** Selected parameters of  $1 \text{ mM} [1\text{H}]^+$  in MeCN in addition of Cl<sub>2</sub>CHCOOH.

![](_page_32_Figure_0.jpeg)

*Results:* The reversible redox wave is assigned to  $[Co^{III}HNi^{II}/Co^{II}HNi^{II}]$  couple,  $i_{pa}/i_{pc} = 0.98$ .

![](_page_32_Figure_2.jpeg)

**Fig. S26** Cyclic voltammogram of  $[1H]^+$  in MeCN. Conditions: ~ 1 mM  $[1H]^+$ , 0.1 M *n*-NBu<sub>4</sub>PF<sub>6</sub>, scan rate = 100 mV/s.

![](_page_33_Figure_0.jpeg)

**Fig. S27** (a) Cyclic voltammogram of  $[1H]^+$  at various scan rate and (b) scan rate dependence of  $i_p$  for the couples  $[1H]^{+/0}$  in MeCN. Conditions: ~ 0.5 mM  $[1H]^+$ , 0.1 M *n*-NBu<sub>4</sub>PF<sub>6</sub>, scan rate = 0.1-0.5 V/s.

![](_page_34_Figure_0.jpeg)

*Results:*  $[1H]^+$  coexists with the excessive Cl<sub>2</sub>CHCOOH in MeCN proves that  $[1H]^+$  is stable in acid condition for the electrochemical reaction.

**Fig. S28** <sup>1</sup>H NMR spectrum of  $[1H]^+$  with the addition of 20  $\mu$ L Cl<sub>2</sub>CHCOOH (the concentration of acid is much higher than that in the electrochemical reaction).

### 4. X-ray crystal structure analysis

	[1Cl] <sup>+</sup>		
Empirical formula	C39H45Cl1CoF6NiP3S2·CH2Cl2		
Formula weight	1022.79		
Temperature / K	293(2)		
Crystal system	monoclinic		
Space group	P2 <sub>1</sub> /n		
<i>a</i> / Å	14.1464(3)		
b / Å	13.3562(4)		
<i>c</i> / Å	25.4313(7)		
α/°	90		
β /°	103.789(2)		
γ / °	90		
Volume / Å <sup>3</sup>	4666.6(2)		
Z	4		
$ ho_{ m calc}$ / g cm <sup>-3</sup>	1.456		
μ / mm <sup>-1</sup>	7.121		
F(000)	2096.0		
$2\Theta$ range for data collection / °	7.158 to 154.344		
	-17≤h≤14,		
Index ranges	-16≤k≤9,		
	-32 <u>≤</u> 1 <u>≤</u> 32		
Reflections collected	28729		
Independent reflections	9191 [ $R_{int} = 0.0606, R_{sigma} = 0.0572$ ]		
Data/restraints/parameters	9191/60/510		
Goodness-of-fit on F <sup>2</sup>	1.067		
Final R indexes [I>2 $\sigma$ (I)]	$R_1 = 0.0956, wR_2 = 0.2144$		
Final R indexes [all data]	$R_1 = 0.1301, wR_2 = 0.2377$		
Largest diff. peak/hole / e Å <sup>-3</sup>	1.18/-1.07		

 Table S2. Crystal data and structure refinement of [1Cl]<sup>+</sup>.

	1
Empirical formula	C <sub>39</sub> H <sub>45</sub> P <sub>2</sub> S <sub>2</sub> CoNi
Formula weight	757.45
Temperature / K	293(2)
Crystal system	monoclinic
Space group	P21/n
<i>a</i> / Å	12.47350(19)
b / Å	15.4030(2)
<i>c</i> / Å	19.4262(3)
α / °	90
$\beta$ /°	106.4521(17)
γ / °	90
Volume / Å <sup>3</sup>	3579.54(10)
Z	4
$ ho_{ m calc}$ / g cm <sup>-3</sup>	1.406
μ / mm <sup>-1</sup>	6.414
F(000)	1584.0
$2\Theta$ range for data collection / °	7.446 to 141.754
	-15≤h≤15,
Index ranges	-18≤k≤18,
	-23≤l≤22
Reflections collected	13897
Independent reflections	$6782 [R_{int} = 0.0276, R_{sigma} = 0.0373]$
Data/restraints/parameters	6782/0/411
Goodness-of-fit on F <sup>2</sup>	1.038
Final R indexes [I>2 $\sigma$ (I)]	$R_1 = 0.0370, wR_2 = 0.0881$
Final R indexes [all data]	$R_1 = 0.0432, wR_2 = 0.0926$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.967/-0.625

**Table S3.** Crystal data and structure refinement of 1.

	[ <b>1</b> H] <sup>+</sup>
Empirical formula	$C_{39}H_{46}BCoF_4NiP_2S_2 \cdot 2CH_2Cl_2$
Formula weight	1014.11
Temperature / K	293(2)
Crystal system	triclinic
Space group	P-1
<i>a</i> / Å	10.9745(5)
b / Å	13.3310(6)
<i>c</i> / Å	17.0646(8)
α / °	78.527(4
$\beta$ /°	79.830(4)
γ / °	69.506(4)
Volume / Å <sup>3</sup>	2276.23(19)
Z	2
$ ho_{ m calc}$ / g cm <sup>-3</sup>	1.480
μ / mm <sup>-1</sup>	7.431
F(000)	1042.0
$2\Theta$ range for data collection / °	8.262 to 153.946
	-13≤h≤10,
Index ranges	-16≤k≤16,
	-20 <u>≤</u> 1 <u>≤</u> 21
Reflections collected	23062
Independent reflections	9066 [ $R_{int} = 0.0523, R_{sigma} = 0.0590$ ]
Data/restraints/parameters	9066/0/514
Goodness-of-fit on F <sup>2</sup>	1.061
Final R indexes [I>2 $\sigma$ (I)]	$R_1 = 0.0715, wR_2 = 0.1854$
Final R indexes [all data]	$R_1 = 0.0874, wR_2 = 0.2049$
Largest diff. peak/hole / e Å <sup>-3</sup>	2.59/-1.65

Table S4. Crystal data and structure refinement of  $[1H]^+$ .

	[1]+		
Empirical formula	$C_{39}H_{45}P_2S_2CoNiBF_4\cdot CH_2Cl_2$		
Formula weight	929.18		
Temperature / K	192.99(10)		
Crystal system	monoclinic		
Space group	P21/n		
<i>a</i> / Å	12.9111(2)		
b / Å	20.1158(4)		
<i>c</i> / Å	16.5430(3)		
α / °	90		
$\beta$ /°	99.543(2)		
γ / °	90		
Volume / Å <sup>3</sup>	4237.04(13)		
Z	4		
$ ho_{ m calc}$ / g cm <sup>-3</sup>	1.457		
μ / mm <sup>-1</sup>	6.797		
F(000)	1916.0		
$2\Theta$ range for data collection / °	4.035 to 74.494		
	-15≤h≤16,		
Index ranges	-25≤k≤21,		
	-19 <u>≤</u> 1 <u>≤</u> 20		
Reflections collected	29630		
Independent reflections	8423 [ $R_{int} = 0.0573$ , $R_{sigma} = 0.0572$ ]		
Data/restraints/parameters	8423/0/483		
Goodness-of-fit on F <sup>2</sup>	1.026		
Final R indexes [I>2 $\sigma$ (I)]	$R_1 = 0.0673, wR_2 = 0.1677$		
Final R indexes [all data]	$R_1 = 0.0850, wR_2 = 0.1838$		
Largest diff. peak/hole / e Å <sup>-3</sup>	1.404/-1.213		

**Table S5.** Crystal data and structure refinement of  $[1]^+$ .

[ <b>1</b> (NCMe)] <sup>2+</sup>		
Empirical formula	C <sub>41</sub> H <sub>48</sub> NP <sub>2</sub> S <sub>2</sub> B <sub>2</sub> F <sub>8</sub> CoNi·4CH <sub>3</sub> CN	
Formula weight	1136.34	
Temperature / K	172.99(10)	
Crystal system	orthorhombic	
Space group	Pca2 <sub>1</sub>	
<i>a</i> / Å	21.9622(9)	
b / Å	11.6996(4)	
<i>c</i> / Å	20.9046(7)	
α / °	90	
$\beta$ /°	90	
γ / °	90	
Volume / Å <sup>3</sup>	5371.4(3)	
Z	4	
$ ho_{ m calc}$ / g cm <sup>-3</sup>	1.405	
$\mu / mm^{-1}$	0.863	
F(000)	2352.0	
$2\Theta$ range for data collection / °	6.842 to 49.996	
	-25≤h≤26,	
Index ranges	-13≤k≤12,	
	<i>-</i> 22 <u>≤</u> 1 <u>≤</u> 24	
Reflections collected	27156	
Independent reflections	8897 [ $R_{int} = 0.0466, R_{sigma} = 0.0466$ ]	
Data/restraints/parameters	8897/0/641	
Goodness-of-fit on F <sup>2</sup>	1.040	
Final R indexes [I>2σ (I)]	$R_1 = 0.0354, wR_2 = 0.0822$	
Final R indexes [all data]	$R_1 = 0.0417, wR_2 = 0.0852$	
Largest diff. peak/hole / e Å <sup>-3</sup>	0.68/-0.37	

**Table S6.** Crystal data and structure refinement of  $[1(NCMe)]^{2+}$ .

	[1Cl] <sup>+</sup>	1	[ <b>1</b> H] <sup>+</sup>
Co1–Ni1	2.9257(16)	2.4722(5)	2.5557(10)
Co1–S1	2.252(2)	2.1947(6)	2.2209(13)
Co1–S2	2.259(2)	2.1820(7)	2.2252(13)
Ni1–S1	2.258(2)	2.2645(7)	2.2221(13)
Ni1-S2	2.2470(19)	2.2268(7)	2.2470(14)
Ni1–P1	2.158(2)	2.1450(7)	2.1459(14)
Ni1–P2	2.1720(19)	2.1605(7)	2.1578(13)
Co1–X	2.316(2), X = Cl	_	1.45(5), X = H
Ni1–X	2.588(2), X = Cl	_	1.91(5), X = H
Co1–Cp* plat	1.699	1.686	1.664

**Table S7**. Selected bond distances (Å) of  $[1Cl]^+$ , 1 and  $[1H]^+$ .

	<b>[1</b> ] <sup>+</sup>	$[1(NCMe)]^{2+}$
Co1–Ni1	2.6572(10)	3.005
Co1–S1	2.2099(12)	2.2465(13)
Co1–S2	2.2154(13)	2.2633(13)
Ni1–S1	2.2389(12)	2.2370(13)
Ni1–S2	2.2293(12)	2.2395(12)
Ni1–P1	2.1799(12)	2.1708(14)
Ni1–P2	2.1779(12)	2.1596(13)
Co1–X		1.942(4), X = N
Co1–Cp* plat	1.693	1.695

**Table S8.** Selected bond distances (Å) of  $[1]^+$  and  $[1(NCMe)]^{2+}$ .

	[1Cl] <sup>+</sup>	$[1H]^+$	1	[1]+	[1(NCMe)] <sup>2+</sup>
Co1-S1-Ni1	80.88(7)	70.23(4)	67.32(2)	73.35(4)	84.19(5)
Co1-S2-Ni1	80.97(7)	69.70(4)	68.21(2)	73.43(4)	83.74(4)
S1-Co1-S2	83.54(8)	88.03(5)	93.22(2)	88.85(5)	83.18(5)
S1-Ni1-S2	83.68(7)	87.46(5)	90.17(2)	87.77(4)	83.94(5)
P1-Ni1-P2	87.27(8)	87.42(5)	89.80(3)	87.28(5)	88.14(5)
Co1–X-Ni1	73.03(7), X = C1	98.331, X = H			76.842 X = N

**Table S9.** Selected angles (deg) of the NiCo complexes.

### References

(1) M. Schmidt, G. G. Hoffmann, J. Organomet. Chem., 1977, 124, C5-C8.

(2) T. Yoshino, H. Ikemoto, S. Matsunaga and M. Kanai, *Angew. Chem. Int. Ed.*, 2013, **52**, 2207–2211.