## Electronic Supplementary Information for

# Migratory insertion and hydrogenation of a bridging azide in thiolate-bridged dicobalt reaction platform

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## **Table of Contents**

I. General Materials and Methods	S2
II. Experimental Procedures and Analytical Data	S3
III. References	S5
IV. X-ray Crystallographic Data	S6
V. NMR Spectra	S13
VI. IR Spectra	S18
VII. ESI-HRMS Spectra	\$22

#### I. General Materials and Methods

**General Consideration.** All manipulations were performed under an argon atmosphere by standard Schlenk techniques unless otherwise specified. All solvents were dried and distilled over an appropriate drying agent under argon. [Cp\*CoI<sub>2</sub>(CO)] was prepared according to literature procedure.<sup>1</sup> EtSH (Energy Chemical), NaOAc (Energy Chemical), NH<sub>4</sub>PF<sub>6</sub> (Energy Chemical), NaN<sub>3</sub> (Aldrich), Na(<sup>15</sup>N=N=N) (Cambridge Isotope Laboratories), and NaBPh<sub>4</sub> (Energy Chemical) are commercial available and used as received without further purification.

**Spectroscopic Measurements.** NMR spectra were recorded on a Brüker 400 Ultra Shield spectrometer. The chemical shifts ( $\delta$ ) are given in parts per million relative to CD<sub>2</sub>Cl<sub>2</sub> (5.31 ppm for <sup>1</sup>H; 53.84 ppm for <sup>13</sup>C). Infrared spectra were recorded on a NEXVSTM FT-IR spectrometer. ESI-HRMS spectra were recorded on a HPLC/Q-Tof micro-spectrometer, except that <sup>15</sup>N-labeled **3[BPh4]** was recorded on an SYNAPT G2-Si spectrometer. Elemental analyses were performed on a Vario EL analyzer.

**X-ray Crystallography Procedures.** Single crystal X-ray diffraction studies were carried out on a Brüker SMART APEX CCD diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Empirical absorption corrections were performed using the SADABS program.<sup>2</sup> All structures were solved by direct methods and refined by full-matrix least-squares procedures on  $F^2$  using SHELXTL 2014.<sup>3</sup> All of the non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were generated and refined in ideal positions.

For **1[BPh4]**, the thermal parameters of I and CO ligands were restrained to be similar with the adjacent atoms due to the substitutional disorder, and the "simu" restraint was used with the deviation being 0.02 to help the refinement. The thermal parameters of CH<sub>2</sub>Cl<sub>2</sub> were restrained to be similar with the adjacent atoms, and the "simu" restraint was used with the deviation being 0.02 to avoid the Hirshfeld Test Diff on C–Cl bonds. The C–Cl bond distances in the solvent CH<sub>2</sub>Cl<sub>2</sub> molecule were fixed at 1.80 Å. For **2[PF6]**, the thermal parameters of the PF<sub>6</sub> anion were restrained to be similar with the adjacent atoms, and the "simu" restraint was used with the deviation being 0.02 to avoid the Hirshfeld Test Diff on 0.02 to avoid the Hirshfeld Test Diff on P–F bonds. For **3[BPh4]**, the thermal parameters of N atom and the SEt ligands were restrained to be similar with the adjacent atoms, and the "delu" restraint was used with the deviation being 0.005 to avoid the Hirshfeld Test Diff on several C–C bonds. The "isor" restraint was used with the deviation being 0.005 on C6

atom to help the refinement. The PLATON SQUEEZE tool was used for the calculation of the disordered solvent contribution to the calculated structure factors.<sup>4</sup>

#### **II. Experimental Procedures and Analytical Data**

Synthesis of  $[Cp*Co(I)(\mu-SEt)_2(CO)CoCp*]I(1[I])$ . To a solution of  $[Cp*CoI_2(CO)]$ (475 mg, 1.00 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and H<sub>2</sub>O (30 mL), EtSH (248 mg, 4.00 mmol) and AcONa (820 mg, 10.00 mmol) were added. The color of the reaction mixture gradually changed from violet-red to brown-red. After stirring at room temperature for 12 h, the organic phase was collected and the aqueous phase was washed with small amount of CH<sub>2</sub>Cl<sub>2</sub>. The combined CH<sub>2</sub>Cl<sub>2</sub> solution was dried over MgSO<sub>4</sub> and filtered. The filtrate was dried under vacuum and washed with small amount of Et<sub>2</sub>O to afford brown powder 1[I] (602 mg, 0.76 mmol, 76%). Crystals of 1[I] were unable to obtain using various available systems, therefore, the anion exchange reaction of 1[I] with NaBPh<sub>4</sub> was performed to give complex 1[BPh<sub>4</sub>] in good yield. Single-crystals of 1[BPh<sub>4</sub>] suitable for X-ray diffraction were obtained from a CH<sub>2</sub>Cl<sub>2</sub> solution layered with *n*-hexane at room temperature.

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm):  $\delta$ 2.55 (m, 2H, S*CH*<sub>2</sub>CH<sub>3</sub>), 2.16 (m, 2H, S*CH*<sub>2</sub>CH<sub>3</sub>), 1.77 (s, 15H, Cp\*-*CH*<sub>3</sub>), 1.62 (s, 15H, Cp\*-*CH*<sub>3</sub>), 1.08 (t, *J* = 7.4 Hz, 6H, SCH<sub>2</sub>*CH*<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm):  $\delta$ 104.03 (CO-*C*), 94.50 (Cp\*-*C*), 35.28 (SEt-*CH*<sub>2</sub>), 17.61 (SEt-*CH*<sub>3</sub>), 11.03 (Cp\*-*CH*<sub>3</sub>). ESI-HRMS (CH<sub>2</sub>Cl<sub>2</sub>): Calcd. For [**1**]<sup>+</sup> 665.0229; Found 665.0209; Calcd. For [**1**-**CO**]<sup>+</sup> 637.0280; Found 637.0305. IR (Film, cm<sup>-1</sup>): 2039 (v<sub>CO</sub>). Anal. Calcd. For C<sub>25</sub>H<sub>40</sub>Co<sub>2</sub>I<sub>2</sub>OS<sub>2</sub>: C, 37.89; H, 5.09. Found: C, 37.52; H, 5.01.

Synthesis of  $[Cp*Co(\mu-SEt)(MeCN)]_2[PF_6]_2$  (2[PF\_6]\_2). The solution of 1[I] (791 mg, 1.00 mmol) and NH<sub>4</sub>PF<sub>6</sub> (652 mg, 4.00 mmol) in MeCN (50 mL) was stirred at room temperature in the air for 2 weeks. After removal of the solvent, the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (50 mL), and dried under vacuum. The solids were washed with Et<sub>2</sub>O (10 mL × 3) to give black product 2[PF<sub>6</sub>]<sub>2</sub> (750 mg, 0.85 mmol, 85%). Crystals suitable for X-ray diffraction were obtained from a CH<sub>2</sub>Cl<sub>2</sub> solution layered with Et<sub>2</sub>O at room temperature.

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm):  $\delta$  2.69 (s, 6H, *CH*<sub>3</sub>CN), 1.85 (q, *J* = 7.4 Hz, 4H, S*CH*<sub>2</sub>CH<sub>3</sub>), 1.44 (s, 30H, Cp\*-*CH*<sub>3</sub>), 1.33 (t, *J* = 7.4 Hz, 6H, SCH<sub>2</sub>*CH*<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm):  $\delta$ 132.94 (MeCN-*CN*), 97.86 (Cp\*-*C*), 27.46 (MeCN-*CH*<sub>3</sub>), 17.13 (SEt-*CH*<sub>2</sub>), 9.67 (Cp\*-*CH*<sub>3</sub>), 4.08 (SEt-*CH*<sub>3</sub>). ESI-HRMS (MeCN): Calcd. For [**2**]<sup>2+</sup>

296.0883; Found 296.0891; Calcd. For [**2–MeCN**]<sup>2+</sup> 275.5750; Found 275.5748; Calcd. For [**2–2MeCN**]<sup>2+</sup> 255.0618; Found 255.0627. Anal. Calcd. For C<sub>28</sub>H<sub>46</sub>Co<sub>2</sub>F<sub>12</sub>N<sub>2</sub>P<sub>2</sub>S<sub>2</sub>: C, 38.10; H, 5.25; N, 3.17. Found: C, 38.07; H, 5.15; N, 3.26.

Synthesis of  $[Cp*Co(\mu-SEt)_2(\mu_{1,1}-\eta^1:\eta^1-N_3)CoCp*][BPh4]$  (3[BPh4]). A solution of 2[PF6]<sub>2</sub> (103 mg, 0.12 mmol) and NaBPh<sub>4</sub> (42 mg, 0.12 mmol) in MeCN (5 mL) was mixed with a solution of NaN<sub>3</sub> (10 mg, 0.15 mmol) in MeOH (5 mL) at room temperature. The reaction mixture was stirred for 6 h, and then dried in vacuum. The crude product was extracted with CH<sub>2</sub>Cl<sub>2</sub> (5 mL), and then dried in vacuum. The solids were washed with Et<sub>2</sub>O (5 mL × 2) to give dark green product **3[BPh4]** (85 mg, 0.10 mmol, 84%). The crystals suitable for X-ray diffraction were obtained from a THF solution layered with Et<sub>2</sub>O at -30 °C.

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm):  $\delta$ 7.30 (br, 8H, Ph-*H*), 7.01 (t, *J* = 7.4 Hz, 8H, Ph-*H*), 6.86 (t, *J* = 7.2 Hz, 4H, Ph-*H*), 3.02 (q, *J* = 7.6 Hz, 2H, SCH<sub>2</sub>CH<sub>3</sub>), 1.91 (q, *J* = 7.6 Hz, 2H, SCH<sub>2</sub>CH<sub>3</sub>), 1.71 (t, *J* = 7.6 Hz, 3H, SCH<sub>2</sub>CH<sub>3</sub>), 1.50 (t, *J* = 7.6 Hz, 3H, SCH<sub>2</sub>CH<sub>3</sub>), 1.39 (s, 30H, Cp\*-CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm):  $\delta$ 136.27 (Ph-*C*), 126.00 (Ph-*C*), 122.08 (Ph-*C*), 92.56 (Cp\*-*C*), 27.29 (SEt-*CH*<sub>2</sub>), 23.02 (SEt-*CH*<sub>2</sub>), 20.23 (SEt-*CH*<sub>3</sub>), 18.43 (SEt-*CH*<sub>3</sub>), 9.20 (Cp\*-*CH*<sub>3</sub>). ESI-HRMS (CH<sub>2</sub>Cl<sub>2</sub>): Calcd. For [**3**]<sup>+</sup> 552.1328; Found 552.1335. IR (Film, cm<sup>-1</sup>): 2046 (v<sub>N3</sub>). Due to the instability of **3**[**BPh4**], the elemental analysis was unable to perform.

A sample of <sup>15</sup>N-labelled **3[BPh4]** was synthesized using an analogous synthetic procedure starting from Na(<sup>15</sup>N=N=N) in 85% yield. <sup>1</sup>H NMR spectrum is similar to that of the unlabeled complex. ESI-HRMS (CH<sub>2</sub>Cl<sub>2</sub>): Calcd. For [<sup>15</sup>N-3]<sup>+</sup> 553.1298; Found 553.1310. IR (Film, cm<sup>-1</sup>): 2039 ( $v_{15N3}$ ).

Synthesis of  $[Cp*Co(\mu-SEt)(\mu-NSEt)CoCp*][BPh_4]$  (4[BPh\_4]). A solution of 3[BPh\_4] (116 mg, 0.13 mmol) in THF (5 mL) was stirred at 60 °C for 10 h, and then dried in vacuum. The crude product was extracted with CH<sub>2</sub>Cl<sub>2</sub> (5 mL), and then dried in vacuum. The resulting solids were washed with Et<sub>2</sub>O (5 mL × 2) to give black product 4[BPh\_4] (81 mg, 0.10 mmol, 72%). Crystals suitable for X-ray diffraction were obtained from a CH<sub>2</sub>Cl<sub>2</sub> solution layered with *n*-hexane at room temperature.

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm):  $\delta$ 7.30 (br, 8H, Ph-*H*), 7.02 (t, *J* = 7.4 Hz, 8H, Ph-*H*), 6.86 (t, *J* = 7.2 Hz, 4H, Ph-*H*), 3.38 (q, *J* = 7.5 Hz, 2H, NS*CH*<sub>2</sub>CH<sub>3</sub>), 1.69 (s, 30H, Cp\*-*CH*<sub>3</sub>), 1.12 (t, *J* = 7.5 Hz, 3H, NSCH<sub>2</sub>*CH*<sub>3</sub>), 0.90 (t, *J* = 7.2 Hz, 3H, SCH<sub>2</sub>*CH*<sub>3</sub>), 0.80 (q, *J* = 7.2 Hz, 2H, S*CH*<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm):  $\delta$ 136.28 (Ph-*C*), 125.96 (Ph-*C*), 122.05 (Ph-*C*), 95.13 (Cp\*-*C*), 48.35 (NSEt-*CH*<sub>2</sub>), 35.69 (NSEt-

*CH*<sub>3</sub>), 19.62 (SEt-*CH*<sub>3</sub>), 11.76 (SEt-*CH*<sub>2</sub>), 10.30 (Cp\*-*CH*<sub>3</sub>). ESI-HRMS (CH<sub>2</sub>Cl<sub>2</sub>): Calcd. For [**4**]<sup>+</sup> 524.1266; Found 524.1253. Anal. Calcd. For C<sub>48</sub>H<sub>60</sub>BCo<sub>2</sub>NS<sub>2</sub>: C, 68.32; H, 7.17; N, 1.66. Found: C, 68.40; H, 7.27; N, 1.57.

Synthesis of  $[Cp*Co(\mu-SEt)_2(\mu_{1,3}-\eta^1:\eta^1-NHNNH)CoCp*][BPh4]$  (5[BPh4]). A solution of 3[BPh4] (131 mg, 0.15 mmol) in THF (15 mL) was stirred for 24 h under 20 atm H<sub>2</sub>, and then dried in vacuum. The crude product was extracted with CH<sub>2</sub>Cl<sub>2</sub> (5 mL), and then dried in vacuum. The solids were washed with Et<sub>2</sub>O (5 mL × 3) to give black solids (110 mg). The solids (7.3 mg) were dissolved in CD<sub>2</sub>Cl<sub>2</sub> (0.6 mL) and ferrocene (3.4 mg) was used as an internal standard for <sup>1</sup>H NMR. Formation of 5[BPh4] (55% NMR yield) and 4[BPh4] (15% NMR yield) were observed by <sup>1</sup>H NMR spectrum. Crystals suitable for X-ray diffraction were obtained from a CH<sub>2</sub>Cl<sub>2</sub> solution layered with *n*-hexane at room temperature.

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm):  $\delta$  8.26 (s, 2H, N*H*), 7.30 (br, 8H, Ph-*H*), 7.03 (t, *J* = 7.3 Hz, 8H, Ph-*H*), 6.86 (t, *J* = 7.1 Hz, 4H, Ph-*H*), 1.44~1.40 (br, 34H, Cp\*-*CH*<sub>3</sub> & S*CH*<sub>2</sub>CH<sub>3</sub>), 1.16 (t, *J* = 7.6 Hz, 6H, SCH<sub>2</sub>*CH*<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm):  $\delta$  136.25 (Ph-*C*), 125.93 (Ph-*C*), 122.02 (Ph-*C*), 94.59 (Cp\*-*C*), 28.90 (SEt-*CH*<sub>2</sub>), 18.00 (SEt-*CH*<sub>3</sub>), 9.11 (Cp\*-*CH*<sub>3</sub>). ESI-HRMS (CH<sub>2</sub>Cl<sub>2</sub>): Calcd. For [**5**]<sup>+</sup> 554.1484; Found 554.1493. IR (Film, cm<sup>-1</sup>): 3306 (v<sub>NH</sub>). Since complexes **5**[**BPh**<sub>4</sub>] and **4**[**BPh**<sub>4</sub>] cannot be separated entirely, the elemental analysis of **5**[**BPh**<sub>4</sub>] was unable to perform.

A sample of D-labelled **5[BPh4]** was synthesized using an analogous synthetic procedure starting from D<sub>2</sub> in 67% <sup>1</sup>H NMR yield. <sup>1</sup>H NMR spectrum is similar to that of the unlabeled complex, except that the resonance at 8.26 ppm disappears. ESI-HRMS (CH<sub>2</sub>Cl<sub>2</sub>): Calcd. For [**D-5**]<sup>+</sup> 556.1609; Found 556.1599. IR (Film, cm<sup>-1</sup>): 2451 (v<sub>ND</sub>).

#### **III. References**

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# IV. X-ray Crystallographic Data

	1[ <b>BPh</b> <sub>4</sub> ]•0.5CH <sub>2</sub> Cl <sub>2</sub>	2[PF <sub>6</sub> ] <sub>2</sub>	3[BPh <sub>4</sub> ]			
Formula	$C_{49.5}H_{61}BClCo_2IOS_2$	$C_{28}H_{46}Co_2F_{12}N_2P_2S_2$	$C_{48}H_{60}BCo_2N_3S_2$			
Formula weight	1027.12	882.59	871.78			
Crystal dimensions (mm <sup>3</sup> )	$0.35 \times 0.27 \times 0.22$	$0.32\times 0.29\times 0.24$	0.30 imes 0.21 imes 0.14			
Crystal system	Triclinic	Monoclinic	Monoclinic			
Space group	P-1	C2/c	P2(1)/c			
a (Å)	8.8838(2)	19.185(2)	9.6350(6)			
b (Å)	21.8060(6)	11.4028(13)	32.469(2)			
c (Å)	25.6046(6)	16.908(2)	14.6586(9)			
α(9	83.6460(10)	90.00	90.00			
β(9	80.2610(10)	99.636(2)	91.9523(14)			
γ(9	86.086(2)	90.00	90.00			
Volume (Å <sup>3</sup> )	4852.4(2)	3646.6(7)	4583.0(5)			
Ζ	4	4	4			
<i>T</i> (K)	298(2)	298(2)	173(2)			
$D_{\text{calcd}}$ (g cm <sup>-3</sup> )	1.406	1.608	1.263			
$\mu (\mathrm{mm}^{-1})$	1.495	1.197	0.850			
F (000)	2108	1808	1840			
No. of rflns. collected	51619	10027	43897			
No. of indep. rflns. $/R_{int}$	17097 / 0.0333	3222 / 0.0369	8080 / 0.0349			
No. of obsd. rflns. $[I_0 > 2\sigma(I_0)]$	12932	2603	6942			
Data / restraints / parameters	17097 / 128 / 992	3222 / 174 / 265	8080 / 24 / 571			
$R_1 / wR_2 [I_0 > 2\sigma(I_0)]$	0.0504 / 0.1226	0.0414 / 0.1039	0.0391 / 0.0993			
$R_1 / wR_2$ (all data)	0.0701 / 0.1297	0.0564 / 0.1104	0.0484 / 0.1037			
GOF (on $F^2$ )	1.015	1.050	0.923			
Largest diff. peak and hole (e $Å^{-3}$ )	0.969 / -0.731	0.782 / -0.542	0.529 / -0.395			
CCDC No.	1437845	1551865	1551839			

Table S1. Crystallographic data for 1[BPh4]•0.5CH<sub>2</sub>Cl<sub>2</sub>, 2[PF<sub>6</sub>]<sub>2</sub> and 3[BPh4].

	<b>4[BPh<sub>4</sub>]•</b> CH <sub>2</sub> Cl <sub>2</sub>	5[BPh4]
Formula	$C_{49}H_{62}BCl_2Co_2NS_2$	$C_{48}H_{62}BCo_2N_3S_2$
Formula weight	928.68	873.79
Crystal dimensions (mm <sup>3</sup> )	$0.40\times 0.19\times 0.11$	$0.34\times 0.17\times 0.10$
Crystal system	Monoclinic	Orthorhombic
Space group	P2(1)/c	Pbcm
a (Å)	13.9953(5)	9.675(3)
b (Å)	14.6819(6)	17.641(5)
c (Å)	23.9801(9)	26.834(7)
α(9	90	90
$\beta$ ( )	97.849(2)	90
γ( <b>9</b>	90	90
Volume (Å <sup>3</sup> )	4881.2(3)	4580(2)
Ζ	4	4
<i>T</i> (K)	298(2)	298(2)
$D_{\text{calcd}}$ (g cm <sup>-3</sup> )	1.264	1.267
$\mu (\text{mm}^{-1})$	0.907	0.851
F (000)	1952	1848
No. of rflns. collected	34973	25793
No. of indep. rflns. $/R_{int}$	8598 / 0.0610	4128 / 0.0442
No. of obsd. rflns. $[I_0 > 2\sigma(I_0)]$	4724	3183
Data / restraints / parameters	8598 / 3 / 500	4128 / 0 / 256
$R_1 / wR_2 [I_0 > 2\sigma(I_0)]$	0.0695 / 0.1478	0.0473 / 0.1330
$R_1/wR_2$ (all data)	0.1280 / 0.1700	0.0654 / 0.1484
GOF (on $F^2$ )	1.026	1.049
Largest diff. peak and hole (e $Å^{-3}$ )	0.945 / -0.799	0.418 / -0.511
CCDC No.	1551840	1551841

 Table S2. Crystallographic data for 4[BPh4]•CH2Cl2 and 5[BPh4].



**Fig. S1.** ORTEP diagram of **1[BPh4]**•0.5CH<sub>2</sub>Cl<sub>2</sub>. One of the two crystallographically independent molecules is shown. Thermal ellipsoids are shown at 50% probability level. The substitutional disordered I and CO ligands, BPh<sub>4</sub> anion, the CH<sub>2</sub>Cl<sub>2</sub> molecule and hydrogen atoms on carbons are omitted for clarity.

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	Molecule 1	Molecule 2		Molecule 1	Molecule 2
Distances (Å)					
Co1 ·· Co2	3.4054(1)	3.3941(1)			
Co1–S1	2.2617(12)	2.2493(12)	Co1–S2	2.2678(12)	2.2495(13)
Co2–S1	2.2604(13)	2.2616(12)	Co2–S2	2.2698(12)	2.2532(12)
Co1-C25	1.764(17)	1.752(8)	Co2–I1	2.643(2)	2.6366(12)
Co1–Cp*1	1.7204(0)	1.7233(0)	Co2–Cp*2	1.7280(0)	1.7204(0)
Angles ( )					
Co1-S1-Co2	97.71(5)	97.60(5)	Co1-S2-Co2	97.26(5)	97.84(5)
Torsion angles ( )					
\$1-Co1Co2-\$2	155.929(4)	157.720(4)			
Dihedral angle ( )					
Cp*1–Cp*2	62.9	64.9			

Table S3. Selected bond distances and angles for 1[BPh<sub>4</sub>]•0.5CH<sub>2</sub>Cl<sub>2</sub>.



Fig. S2. ORTEP diagram of  $2[PF_6]_2$ . Thermal ellipsoids are shown at 50% probability level. The PF<sub>6</sub> anions and hydrogen atoms on carbons are omitted for clarity.

Distances (Å)			
Co1 ·· Co1A	3.3624(4)		
Co1–S1	2.2623(9)	Co1–N1	1.914(3)
Co1–Cp*1	1.7021(0)		
Angles ( )			
Co1–S1–Co1A	96.10(4)	Co1-N1-C13	165.9(3)
Torsion angles ( )			
S1-Co1Co1A-S1A	156.644(5)		
Dihedral angles ( )			
Cp*1–Cp*2	61.1		

Table S4. Selected bond distances and angles for 2[PF6]2.



**Fig. S3.** ORTEP diagram of **3[BPh4]** at 173 K. Thermal ellipsoids are shown at 50% probability level. BPh4 anion and hydrogen atoms on carbons are omitted for clarity.

Distances (Å)			
Co1–Co2	2.8483(4)		
Co1–S1	2.3381(14)	Co1–S1'	2.2456(11)
Co1–S2	2.1933(15)	Co1–S2'	2.3261(12)
Co2–S1	2.3115(14)	Co2–S1'	2.2638(12)
Co2–S2	2.2179(14)	Co2–S2'	2.2952(12)
Co1–N1	2.026(5)	Co1–N1'	2.011(4)
Co2–N1	2.044(5)	Co2–N1'	2.014(4)
N1-N2	1.162(9)	N1'-N2'	1.205(6)
N2-N3	1.167(9)	N2'-N3'	1.143(7)
Co1–Cp*1	1.6851(0)	Co2–Cp*2	1.6824(0)
Angles ( )			
Co1-S1-Co2	75.55(4)	Co1–S1'–Co2	78.34(4)
Co1-S2-Co2	80.43(5)	Co1–S2'–Co2	76.10(4)
Co1–N1–Co2	88.8(2)	Co1–N1'–Co2	90.10(18)
Co1-N1-N2	120.8(5)	Co1-N1'-N2'	117.9(4)
N1-N2-N3	176.3(8)	N1'-N2'-N3'	171.9(6)
Torsion angles ( )			
S1-Co2Co1-N1	111.844(3)	S1'-Co2Co1-N1'	125.147(4)
S2-Co1Co2-N1	132.627(4)	S2'-Co1Co2-N1'	119.283(3)
S1-Co1Co2-S2	115.529(3)	S1'-Co1Co2-S2'	115.571(3)
Dihedral angle ( )			
Cp*1–Cp*2	7.6		

Table S5. Selected bond distances and angles for 3[BPh4].



**Fig. S4.** ORTEP diagram of **4[BPh**<sub>4</sub>]•CH<sub>2</sub>Cl<sub>2</sub>. Thermal ellipsoids are shown at 50% probability level. The BPh<sub>4</sub> anion, the CH<sub>2</sub>Cl<sub>2</sub> molecule and hydrogen atoms on carbons are omitted for clarity.

Distances (Å)			
Co1–Co2	2.4668(10)		
Co1–S1	2.2308(18)	Co2–S1	2.2176(18)
Co1–N1	1.815(4)	Co2–N1	1.790(5)
N1-S2	1.605(5)		
Co1–Cp*1	1.6942(0)	Co2–Cp*2	1.6938(0)
Angles ( )			
Co1-S1-Co2	67.36(5)	Co1–N1–Co2	86.3(2)
Co1-N1-S2	144.9(3)	Co2-N1-S2	126.6(3)
Torsion angles ( )			
S1-Co1Co2-N1	124.784(2)	Co1–Co2N1–S2	166.644(4)
Dihedral angle ( )			
Cp*1–Cp*2	52.2		

Table S6.	. Selected	bond	distances	and a	angles	for	4[BPh	4]•(	$CH_2C$	Ľl <sub>2</sub> .
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**Fig. S5.** ORTEP diagram of **5**[**BPh**<sub>4</sub>]. Thermal ellipsoids are shown at 50% probability level. The BPh<sub>4</sub> anion and hydrogen atoms on carbons are omitted for clarity.

Distances (Å)			
Co1 ·· Co1A	3.1475(8)		
Co1–S1	2.2272(11)	Co1–S2	2.2353(10)
Co1–N1	1.905(3)	N1-N2	1.286(3)
Co1–Cp*1	1.6996(2)		
Angles ( )			
Co1–S1–Co1A	89.92(5)	Co1–S2–Co1A	89.51(5)
Co1-N1-N2	135.2(2)	N1N2N1A	118.1(4)
Torsion angles ( )			
S1-Co1Co1A-S2	145.827(12)		
Dihedral angle ( )			
Cp*1–Cp*2	44.6		

Table S7. Selected bond distances and angles for 5[BPh4].

### V. NMR Spectra





Fig. S7.  $^{13}$ C NMR spectrum of 1[I] in CD<sub>2</sub>Cl<sub>2</sub>.





Fig. S8. <sup>1</sup>H NMR spectrum of 2[PF6]2 in CD<sub>2</sub>Cl<sub>2</sub>.

Fig. S9. <sup>13</sup>C NMR spectrum of  $2[PF_6]_2$  in CD<sub>2</sub>Cl<sub>2</sub>.





Fig. S10. <sup>1</sup>H NMR spectrum of 3[BPh4] in CD<sub>2</sub>Cl<sub>2</sub>.







Fig. S12 <sup>1</sup>H NMR spectrum of 4[BPh4] in CD<sub>2</sub>Cl<sub>2</sub>.

Fig. S13. <sup>13</sup>C NMR spectrum of 4[BPh4] in CD<sub>2</sub>Cl<sub>2</sub>.





Fig. S14. <sup>1</sup>H NMR spectrum of 5[BPh4] in CD<sub>2</sub>Cl<sub>2</sub>.

Fig. S15. <sup>13</sup>C NMR spectrum of 5[BPh4] in CD<sub>2</sub>Cl<sub>2</sub>.





Fig. S16. <sup>1</sup>H NMR spectrum of D-5[BPh4] in CD<sub>2</sub>Cl<sub>2</sub>.

## VI. IR Spectra





Fig. S18. IR spectrum of 2[PF6]2.



Fig. S19. IR spectrum of 3[BPh4].





Fig. S20. IR spectrum of <sup>15</sup>N-3[BPh4].





Fig. S22. IR spectrum of 5[BPh4].



Fig. S23. IR spectrum of D-5[BPh4].



#### VII. ESI-HRMS Spectra

Fig. S24. ESI-HRMS spectrum of 1[I] in CH<sub>2</sub>Cl<sub>2</sub>.

(a) The signals at m/z = 665.0209 and 637.0305 corresponds to  $[1]^+$  and  $[1-CO]^+$ , respectively. (b) Calculated isotopic distribution (upper) and the amplifying experimental diagram for  $[1]^+$  (bottom). (c) Calculated isotopic distribution (upper) and the amplifying experimental diagram for  $[1-CO]^+$ , (bottom).







(a) The signals at m/z = 296.0891, 275.5748 and 255.0627 corresponds to  $[2]^{2+}$ ,  $[2-MeCN]^{2+}$  and  $[2-2MeCN]^{2+}$ , respectively. (b) Calculated isotopic distribution (upper) and the amplifying experimental diagram for  $[2]^{2+}$  (bottom). (c) Calculated isotopic distribution (upper) and the amplifying experimental diagram for  $[2-MeCN]^{2+}$  (bottom). (d) Calculated isotopic distribution (upper) and the amplifying experimental diagram for  $[2-MeCN]^{2+}$  (bottom). (d) Calculated isotopic distribution (upper) and the amplifying experimental diagram for  $[2-2MeCN]^{2+}$  (bottom).

(a)





S24



Fig. S26. ESI-HRMS spectrum of 3[BPh4] in CH<sub>2</sub>Cl<sub>2</sub>.

(a) The signal at an m/z = 552.1335 corresponds to  $[3]^+$ . (b) Calculated isotopic distribution (upper) and the amplifying experimental diagram for  $[3]^+$  (bottom).





Fig. S27. ESI-HRMS spectrum of <sup>15</sup>N-3[BPh4] in CH<sub>2</sub>Cl<sub>2</sub>.

(a) The signal at an m/z = 553.1310 corresponds to <sup>15</sup>N-[3]<sup>+</sup>. (b) Calculated isotopic distribution (upper) and the amplifying experimental diagram for <sup>15</sup>N-[3]<sup>+</sup> (bottom).





Fig. S28. ESI-HRMS spectrum of 4[BPh4] in CH<sub>2</sub>Cl<sub>2</sub>.

(a) The signal at an m/z = 524.1253 corresponds to [4]<sup>+</sup>. (b) Calculated isotopic distribution (upper) and the amplifying experimental diagram for [4]<sup>+</sup> (bottom).
(a)





Fig. S29. ESI-HRMS spectrum of 5[BPh4] in CH<sub>2</sub>Cl<sub>2</sub>.

(a) The signal at an m/z = 554.1493 corresponds to  $[5]^+$ . (b) Calculated isotopic distribution (upper) and the amplifying experimental diagram for  $[5]^+$  (bottom).





Fig. S30. ESI-HRMS spectrum of D-5[BPh4] in CH<sub>2</sub>Cl<sub>2</sub>.

(a) The signal at an m/z = 556.1599 corresponds to **D-[5]**<sup>+</sup>. (b) Calculated isotopic distribution (upper) and the amplifying experimental diagram for **D-[5]**<sup>+</sup> (bottom). (a)



(b)

