

# Syntheses and properties of NCN-bridged tri- and tetranuclear complexes of cobalt and rhodium

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## Abstract

The reaction of  $[\text{Cp}^*\text{CoI}_2]_2$  (**1b**) with 2 equiv of NaNCNH affords the 16-membered macrocyclic NCNH-bridged tetracobalt(III) complex  $[\text{Cp}^*\text{CoI}(\mu_2\text{-NCNH-}N,N')]_4$  (**2b**), while that with 2 equiv of  $\text{Na}_2\text{NCN}$  yields the  $C_3$ -elongated cubane-like NCN-bridged tetracobalt(III) complex  $[\text{Cp}^*\text{Co}(\mu_3\text{-NCN-}N,N,N')_3(\text{CoCp}^*)_3(\mu_3\text{-NCN-}N,N,N)]$  (**4b**). Treatment of  $[\text{Cp}^*\text{RhCl}_2]_2$  (**1c**) with 2 equiv of NaNCNH gives the  $C_3$ -elongated cubane-like tetrarhodium(III) complex  $[\text{Cp}^*\text{Rh}(\mu_3\text{-NCN-}N,N,N')_3(\text{RhCp}^*)_3(\mu_3\text{-NCN-}N,N,N)]$  (**4c**) via the macrocyclic complex  $[\text{Cp}^*\text{RhCl}(\mu_2\text{-NCNH-}N,N')]_4$  (**2c**). On the other hand, the reaction of  $[\text{Cp}^*\text{CoCl}_2]$  (**7**) with  $\text{Na}_2\text{NCN}$  affords the anionic bis(NCN)-capped tricobalt(II) complex  $\text{Na}[(\text{Cp}^*\text{Co})_3(\mu_3\text{-NCN-}N,N,N)_2]$  (**6**). The molecular structures of complexes **2b** ·  $\text{CH}_2\text{Cl}_2$  and **4c** ·  $2\text{C}_6\text{H}_6$  have been confirmed by X-ray analyses. The electrochemical properties of these types of NCN-bridged group 9 metal complexes have also been examined.

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**Keywords:** Cyanamide; Cobalt; Rhodium; Iridium; Cluster; Redox

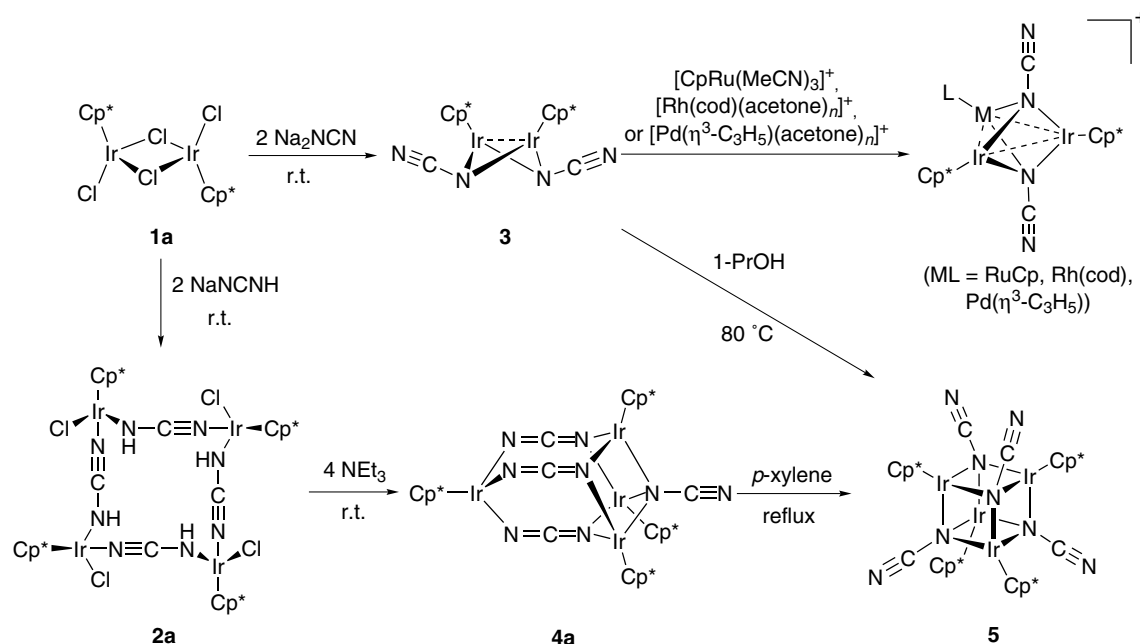
## 1. Introduction

Recent studies on the polynuclear transition metal complexes with nitrogen-based bridging ligands such as cyano or azido have revealed that these ligands can act as effective glue to construct nano-scaled polymetallic molecular cages which sometimes serve as host molecules, molecular semiconductors, and molecular magnets [1]. Although cyanamide anions ( $\text{NCN}^{2-}$  and  $\text{NCNH}^-$ ) are among such molecules to be expected to work as unique bridging ligands for the construction of polynuclear systems owing to their soft, sterically small, and potentially polydentate nature, transition metal complexes with NCN- [2] or NCNH-bridges [3] have poorly been explored. Recently we have shown that the diiridium(III) complex  $[\text{Cp}^*\text{IrCl}_2]_2$  (**1a**,

$\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) reacts with NaNCNH or  $\text{Na}_2\text{NCN}$  to afford the 16-membered macrocyclic NCNH-bridged tetrairidium complex  $[\text{Cp}^*\text{IrCl}(\mu_2\text{-NCNH-}N,N')]_4$  (**2a**) or the NCN-bridged diiridium complex  $[\text{Cp}^*\text{Ir}(\mu_2\text{-NCN-}N,N)]_2$  (**3**), respectively, which can further be converted into the  $C_3$ -elongated cubane-like NCN-bridged tetrairidium complex  $[\text{Cp}^*\text{Ir}(\mu_3\text{-NCN-}N,N,N')_3(\text{IrCp}^*)_3(\mu_3\text{-NCN-}N,N,N)]$  (**4a**), the regular cubane-type NCN-bridged tetrairidium complex  $[\text{Cp}^*\text{Ir}(\mu_3\text{-NCN-}N,N,N)]_4$  (**5**) and the heterotrinnuclear complexes  $[(\text{Cp}^*\text{Ir})_2(\text{ML})(\mu_3\text{-NCN-}N,N,N)_2]^+$  ( $\text{ML} = \text{RuCp}$ ,  $\text{Rh}(\text{cod})$ ,  $\text{Pd}(\eta^3\text{-C}_3\text{H}_5)$ ;  $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ;  $\text{cod} = \text{cyclo-octa-1,5-diene}$ ) (Scheme 1) [4]. In this study, we have synthesized cobalt and rhodium analogues of the 16-membered macrocyclic and  $C_3$ -elongated cubane-like complexes,  $[\text{Cp}^*\text{CoI}(\mu_2\text{-NCNH-}N,N')]_4$  (**2b**) and  $[\text{Cp}^*\text{M}(\mu_3\text{-NCN-}N,N,N')_3(\text{MCp}^*)_3(\mu_3\text{-NCN-}N,N,N)]$  ( $\text{M} = \text{Co}$  (**4b**),  $\text{Rh}$  (**4c**)), as well as the anionic bis(NCN)-capped tricobalt(II) complex  $\text{Na}[(\text{Cp}^*\text{Co})_3(\mu_3\text{-NCN-}N,N,N)_2]$  (**6**), and have compared their chemical properties.

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Scheme 1. Transformation of NCNH- and NCN-bridged di- and tetrairidium complexes.

## 2. Experimental

### 2.1. General considerations

All reactions were carried out under a dry dinitrogen atmosphere using standard Schlenk techniques unless otherwise specified.  $[\text{Cp}^*\text{CoI}_2]$  (**1b**) [5],  $[\text{Cp}^*\text{RhCl}_2]$  (**1c**) [6],  $[\text{Cp}^*\text{CoCl}_2]$  (**7**) [7], and  $\text{NaNCNH}$  [8] were prepared according to the literature methods. Solvents were dried by common procedures and degassed before use. Other reagents were commercially obtained and used as received.  $^1\text{H}$  NMR spectra were recorded on a JEOL ECA-500 spectrometer ( $^1\text{H}$ , 500 MHz). IR spectra were recorded on a JASCO FT/IR-410 spectrometer. Elemental analyses were performed on a Perkin Elmer 2400 series II CHN analyzer. Amounts of the solvent molecules in the crystals were determined not only by elemental analyses but also by  $^1\text{H}$  NMR spectroscopy.

### 2.2. Synthesis of $[\text{Cp}^*\text{CoI}(\mu_2\text{-NCNH-}N,N,N')]_4$ (**2b**)

Complex **1b** (78.0 mg, 0.087 mmol) and  $\text{NaNCNH}$  (10.5 mg, 0.164 mmol) were dissolved in tetrahydrofuran (4 mL) and stirred for 1 day at room temperature. The resulting dark green suspension was dried *in vacuo*, and the resulting dark green powder was extracted with benzene until the filtrate became colorless. The combined filtrate was evaporated to dryness, and the residue was dissolved in dichloromethane–toluene. Slow diffusion of diethyl ether into this solution gave dark green block crystals of  $[\text{Cp}^*\text{CoI}(\mu_2\text{-NCNH-}N,N,N')]_4 \cdot \text{CH}_2\text{Cl}_2$  (**2b** ·  $\text{CH}_2\text{Cl}_2$ ), which were suitable for crystallographic study. A part of dichloromethane in the crystals was lost

by drying *in vacuo* to yield a black powder with the empirical formula **2b** ·  $0.5\text{CH}_2\text{Cl}_2$  (33.9 mg, 0.023 mmol, 55% yield).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 3.58 (br, 4H, NH), 1.49 (s, 60H, Cp\*). IR (KBr,  $\text{cm}^{-1}$ ): 3271 (w, NH), 2203 (s, NCN), 1206 (m, NCN). Anal. Calc. for  $\text{C}_{44.5}\text{H}_{65}\text{Cl}\text{-Co}_4\text{I}_4\text{N}_8$ : C, 35.85; H, 4.39; N, 7.52. Found: C, 35.84; H, 4.04; N, 7.68%.

### 2.3. Synthesis of $[\text{Cp}^*\text{Co}(\mu_3\text{-NCN-}N,N,N')]_3(\text{CoCp}^*)_3$ ( $\mu_3\text{-NCN-}N,N,N'$ ) (**4b**)

Complex **1b** (133.3 mg, 0.149 mmol) and  $\text{Na}_2\text{NCN}$  (43.4 mg, 0.505 mmol) were dissolved in methanol (4 mL) and stirred for 17 h at room temperature. The resulting black suspension was dried *in vacuo*, and the black precipitate was extracted with benzene using a Soxhlet apparatus. Evaporation of benzene gave  $[\text{Cp}^*\text{Co}(\mu_3\text{-NCN-}N,N,N')]_3(\text{CoCp}^*)_3(\mu_3\text{-NCN-}N,N,N')$  (**4b**) as an air-sensitive black powder (33.2 mg, 0.035 mmol, 48% yield).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 1.39 (s, 15H, Cp\*), 1.35 (s, 45H, Cp\*). IR (KBr,  $\text{cm}^{-1}$ ): 2068 (m, NCN), 1997 (s, NCN), 1154 (m, NCN). Anal. Calc. for  $\text{C}_{44}\text{H}_{60}\text{Co}_4\text{N}_8$ : C, 56.42; H, 6.46; N, 11.96. Found: C, 56.97; H, 6.64; N, 11.67%.

### 2.4. Transformation of **2b** into **4b**

Complex **2b** ·  $0.5\text{CH}_2\text{Cl}_2$  (47.8 mg, 0.032 mmol) and  $\text{Na}_2\text{NCN}$  (22.0 mg, 0.256 mmol) were dissolved in methanol (4 mL) and stirred for 1 day at room temperature until the color of the solution changed from dark green to opaque black. The reaction mixture was dried *in vacuo* to give a black powder, which was extracted with benzene using a Soxhlet apparatus. Evaporation of the solvent gave

[Cp\*Co( $\mu_3$ -NCN-*N,N,N'*)<sub>3</sub>(CoCp\*)<sub>3</sub>( $\mu_3$ -NCN-*N,N,N'*)] (**4b**) as a black powder (11.1 mg, 0.012 mmol, 37% yield).

### 2.5. Synthesis of [Cp\*Rh( $\mu_3$ -NCN-*N,N,N'*)<sub>3</sub>(RhCp\*)<sub>3</sub>( $\mu_3$ -NCN-*N,N,N'*)] (**4c**)

Complex **1c** (81.5 mg, 0.132 mmol) and Na<sub>2</sub>NCN (36.3 mg, 0.422 mmol) were dissolved in methanol (4 mL) and stirred for 1 day at room temperature until the orange solution turned brown. The resulting solution was evaporated to dryness, and the brown precipitate was extracted with benzene until the filtrate became colorless. The extract was dried *in vacuo* to give a fine brown powder, which was dissolved in toluene–benzene. Layering hexane over this brown solution at –40 °C gave dark brown crystals of [Cp\*Rh( $\mu_3$ -NCN-*N,N,N'*)<sub>3</sub>(RhCp\*)<sub>3</sub>( $\mu_3$ -NCN-*N,N,N'*)]·2C<sub>6</sub>H<sub>6</sub> (**4c**·2C<sub>6</sub>H<sub>6</sub>), which were suitable for X-ray study. The crystals gave off 1.5 moles of benzene when dried *in vacuo* to afford a brown powder with the empirical formula **4c**·0.5C<sub>6</sub>H<sub>6</sub> (68.8 mg, 0.060 mmol, 91% yield). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ ): 1.57 (s, 45H, Cp\*), 1.55 (s, 15H, Cp\*). IR (KBr, cm<sup>-1</sup>): 2054 (m, NCN), 2007 (s, NCN), 1146 (m, NCN). Anal. Calc. for C<sub>47</sub>H<sub>63</sub>N<sub>8</sub>Rh<sub>4</sub>: C, 49.02; H, 5.51; N, 9.73. Found: C, 49.12; H, 5.64; N, 9.72%.

### 2.6. Synthesis of Na[(Cp\*Co)<sub>3</sub>( $\mu_3$ -NCN-*N,N,N'*)<sub>2</sub>] (**6**)

#### 2.6.1. Method 1

Complex **7** (1.51 g, 3.29 mmol) and Na<sub>2</sub>NCN (733.3 mg, 8.53 mmol) were dissolved in methanol (30 mL) and stirred for 1 day at room temperature until a dark black suspension was obtained. The resulting suspension was dried *in vacuo* and was extracted with dichloromethane. The filtrate was evaporated to dryness and was recrystallized from dichloromethane–hexane to afford a highly efflorescent black rhombic crystals, which gave off some dichloromethane when dried *in vacuo* to yield Na[(Cp\*Co)<sub>3</sub>( $\mu_3$ -NCN-*N,N,N'*)<sub>2</sub>]·0.5CH<sub>2</sub>Cl<sub>2</sub> (**6**·0.5CH<sub>2</sub>Cl<sub>2</sub>) as a black powder (987.9 mg, 1.357 mmol, 62% yield). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ ): 20.52 (br, Cp\*). EPR (CH<sub>2</sub>Cl<sub>2</sub>, –150 °C): *g* = 2.05. IR (KBr, cm<sup>-1</sup>): 2116 (s, NCN), 1146 (m, NCN). Anal. Calc. for C<sub>32.5</sub>H<sub>46</sub>ClCo<sub>3</sub>N<sub>4</sub>Na: C, 53.62; H, 6.37; N, 7.70. Found: C, 53.42; H, 6.48; N, 8.25%.

#### 2.6.2. Method 2

Complex **7** (1.71 g, 3.72 mmol) and NaNCNH (1.01 g, 15.8 mmol) were dissolved in methanol (30 mL) and stirred for 1 day at room temperature until a black suspension was obtained. The resulting suspension was dried *in vacuo* and was dissolved in benzene. The solution was filtered through Celite 545, and the filtrate was evaporated to dryness. The residue was recrystallized from 1,2-dichloroethane–hexane to afford a highly efflorescent black needles, which gave off some 1,2-dichloroethane when dried *in vacuo* to yield a black powder with the empirical formula **6**·0.75C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> (923.9 mg, 1.216 mmol, 49% yield). Anal. Calc. for

C<sub>33.5</sub>H<sub>48</sub>Cl<sub>1.5</sub>Co<sub>3</sub>N<sub>4</sub>Na: C, 52.96; H, 6.37; N, 7.37. Found: C, 53.11; H, 6.41; N, 6.94%.

### 2.7. X-ray diffraction studies of **2b**·CH<sub>2</sub>Cl<sub>2</sub> and **4c**·2C<sub>6</sub>H<sub>6</sub>

Diffraction data for **2b**·CH<sub>2</sub>Cl<sub>2</sub> and **4c**·2C<sub>6</sub>H<sub>6</sub> were collected on a Rigaku Mercury CCD area detector with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71070 Å) at –150 °C. Intensity data were corrected for empirical absorption (REQAB) [9] and for Lorentz and polarization effects. A correction for secondary extinction was further applied (coefficient, **2b**·CH<sub>2</sub>Cl<sub>2</sub>: 152.66, **4c**·2C<sub>6</sub>H<sub>6</sub>: 45.035) [10]. The structure solution and refinements were carried out by using the *CrystalStructure* package [11]. The positions of the non-hydrogen atoms were determined by heavy atom Patterson methods (SHELX-97) [12] and subsequent Fourier syntheses (DIRDIF99) [13]. All the non-hydrogen atoms were refined on *F*<sub>o</sub> (*I* > 3 $\sigma$ (*I*)) by full-matrix least squares techniques with anisotropic thermal parameters, while all the hydrogen atoms were placed at the calculated positions with fixed isotropic parameters. The atomic scattering factors were taken from Ref. [14]. Anomalous dispersion effects were included in *F*<sub>c</sub> [15].

Table 1

X-ray crystallographic data for complexes **2b**·CH<sub>2</sub>Cl<sub>2</sub> and **4c**·2C<sub>6</sub>H<sub>6</sub>

|  | <b>2b</b> ·CH <sub>2</sub> Cl <sub>2</sub>  | <b>4c</b> ·2C <sub>6</sub> H <sub>6</sub>                      |
|--|---|--|
| Chemical formula   | C <sub>45</sub> H <sub>66</sub> Cl <sub>2</sub> Co <sub>4</sub> I <sub>4</sub> N <sub>8</sub> | C <sub>56</sub> H <sub>72</sub> N <sub>8</sub> Rh <sub>4</sub> |
| Formula weight   | 1533.33   | 1268.86  |
| Crystal color, habit, behavior   | Dark green, block, efflorescent   | Dark brown, block, efflorescent                                |
| Dimensions of crystal  | 1.20 × 1.00 × 0.80  | 0.20 × 0.20 × 0.20   |
| Crystal system   | Orthorhombic  | Triclinic  |
| Space group  | <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>   | <i>P</i> $\bar{1}$   |
| <i>a</i> (Å)   | 13.0631(9)  | 12.027(3)  |
| <i>b</i> (Å)   | 13.2121(11)   | 13.028(3)  |
| <i>c</i> (Å)   | 32.388(3)   | 18.965(6)  |
| $\alpha$ (°)   |   | 78.23(2)   |
| $\beta$ (°)  |   | 85.14(2)   |
| $\gamma$ (°)   |   | 64.88(1)   |
| <i>V</i> (Å <sup>3</sup> )   | 5589.9(8)   | 2634.1(12)   |
| <i>Z</i>   | 4   | 2  |
| $\rho_{\text{calcd}}$ (g cm <sup>-3</sup> )                              | 1.822   | 1.600  |
| <i>F</i> (000)   | 2984  | 1288   |
| $\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )                               | 35.10   | 12.73  |
| Trans. factors range   | 0.3320–1.0000   | 0.8162–1.0000  |
| 2 $\theta$ Range (°)   | 5 < 2 $\theta$ < 55   | 5 < 2 $\theta$ < 55  |
| No. reflections measured   | 34,318  | 19,746   |
| No. unique reflections   | 6608  | 11,365   |
| <i>R</i> <sub>int</sub>  | 0.053   | 0.034  |
| No. reflections used ( <i>I</i> > 3 $\sigma$ ( <i>I</i> ))               | 4931  | 6395   |
| No. parameters refined   | 636   | 686  |
| Flack parameter  | 0.03(6)   | –  |
| <i>R</i> ( <i>I</i> > 3 $\sigma$ ( <i>I</i> )) <sup>a</sup>              | 0.054   | 0.035  |
| <i>R</i> <sub>w</sub> ( <i>I</i> > 3 $\sigma$ ( <i>I</i> )) <sup>b</sup> | 0.056   | 0.036  |
| GOF ( <i>I</i> > 3 $\sigma$ ( <i>I</i> )) <sup>c</sup>                   | 1.000   | 1.000  |

<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ .

<sup>b</sup>  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$ ,  $w = [pF_o^2 + q\sigma(F_o^2)]^{-1}$  [ $p = 0.0002$  (**2b**·CH<sub>2</sub>Cl<sub>2</sub>), 0 (**4c**·2C<sub>6</sub>H<sub>6</sub>);  $q = 1.4450$  (**2b**·CH<sub>2</sub>Cl<sub>2</sub>), 0.8020 (**4c**·2C<sub>6</sub>H<sub>6</sub>)].

<sup>c</sup>  $\text{GOF} = [\sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{params}})]^{1/2}$ .

Table 2  
Selected bond lengths (Å) and angles (°) for **2b** · CH<sub>2</sub>Cl<sub>2</sub>

|            |         |                 |        |
|------------|---------|-----------------|--------|
| Co(1)–N(1) | 1.92(1) | Co(1)–N(1)–C(1) | 165(1) |
| Co(2)–N(3) | 1.92(1) | Co(2)–N(3)–C(2) | 171(1) |
| Co(3)–N(5) | 1.93(1) | Co(3)–N(5)–C(3) | 173(1) |
| Co(4)–N(7) | 1.90(1) | Co(4)–N(7)–C(4) | 167(1) |
| Co(1)–N(8) | 1.95(1) | Co(2)–N(2)–C(1) | 121(1) |
| Co(2)–N(2) | 1.97(1) | Co(3)–N(4)–C(2) | 116(1) |
| Co(3)–N(4) | 1.98(1) | Co(4)–N(6)–C(3) | 117(1) |
| Co(4)–N(6) | 1.98(1) | Co(1)–N(8)–C(4) | 117(1) |
| N(1)–C(1)  | 1.15(2) | N(1)–C(1)–N(2)  | 170(1) |
| N(3)–C(2)  | 1.13(2) | N(3)–C(2)–N(4)  | 175(1) |
| N(5)–C(3)  | 1.11(2) | N(5)–C(3)–N(6)  | 174(1) |
| N(7)–C(4)  | 1.18(2) | N(7)–C(4)–N(8)  | 172(1) |
| N(2)–C(1)  | 1.28(2) |                 |        |
| N(4)–C(2)  | 1.32(2) |                 |        |
| N(6)–C(3)  | 1.32(2) |                 |        |
| N(8)–C(4)  | 1.29(2) |                 |        |

The values of  $\Delta f'$  and  $\Delta f''$  were taken from Ref. [16]. The maximum and minimum residual peaks on the final difference Fourier maps were 1.70/–1.00 and 0.79/–0.65 for **2b** · CH<sub>2</sub>Cl<sub>2</sub> and **4c** · 2C<sub>6</sub>H<sub>6</sub>, respectively. Details of the X-ray diffraction study are summarized in Table 1, and the selected bond lengths and angles for **2b** · CH<sub>2</sub>Cl<sub>2</sub> and **4c** · 2C<sub>6</sub>H<sub>6</sub> are listed in Tables 2 and 3, respectively.

### 2.8. Electrochemical properties of complexes 3–6

Cyclic voltammetry studies were performed with a BAS CV-50W analyzer. Potentials were measured at a glassy carbon working electrode in dichloromethane solution containing 0.1 M NBu<sub>4</sub><sup>+</sup>BF<sub>4</sub><sup>–</sup> and 2 mM sample at 25 °C. The reduction and oxidation potentials vs. SCE ( $E_{1/2}$ ) and the peak currents ratios ( $i_{p,c}/i_{p,a}$ ) of complexes **3–6** are summarized in Table 4. The cyclic voltammograms for complexes **4a**, **5**, and **6** are shown in Figs. 3 and 4.

Table 3  
Selected bond lengths (Å) and angles (°) for **4c** · 2C<sub>6</sub>H<sub>6</sub>

|            |          |                  |          |
|------------|----------|------------------|----------|
| Rh(1)–N(1) | 2.103(6) | Rh(1)–N(1)–C(1)  | 123.1(6) |
| Rh(1)–N(3) | 2.121(6) | Rh(1)–N(3)–C(2)  | 121.0(5) |
| Rh(1)–N(5) | 2.117(5) | Rh(1)–N(5)–C(3)  | 120.8(5) |
| Rh(3)–N(2) | 2.080(4) | Rh(3)–N(2)–C(1)  | 121.6(4) |
| Rh(2)–N(2) | 2.080(5) | Rh(2)–N(2)–C(1)  | 119.2(4) |
| Rh(2)–N(4) | 2.081(6) | Rh(2)–N(4)–C(2)  | 121.0(5) |
| Rh(4)–N(4) | 2.074(5) | Rh(4)–N(4)–C(2)  | 120.0(4) |
| Rh(4)–N(6) | 2.094(6) | Rh(4)–N(6)–C(3)  | 121.8(4) |
| Rh(3)–N(6) | 2.088(6) | Rh(3)–N(6)–C(3)  | 119.0(5) |
| Rh(2)–N(7) | 2.168(5) | Rh(2)–N(2)–Rh(3) | 105.1(2) |
| Rh(3)–N(7) | 2.161(5) | Rh(2)–N(4)–Rh(4) | 105.3(2) |
| Rh(4)–N(7) | 2.171(6) | Rh(3)–N(6)–Rh(4) | 104.1(2) |
| N(1)–C(1)  | 1.192(7) | Rh(2)–N(7)–C(4)  | 116.9(4) |
| N(3)–C(2)  | 1.203(7) | Rh(3)–N(7)–C(4)  | 118.3(4) |
| N(5)–C(3)  | 1.208(7) | Rh(4)–N(7)–C(4)  | 120.0(5) |
| N(2)–C(1)  | 1.263(7) | Rh(2)–N(7)–Rh(3) | 99.4(2)  |
| N(4)–C(2)  | 1.256(7) | Rh(3)–N(7)–Rh(4) | 99.2(2)  |
| N(6)–C(3)  | 1.263(7) | Rh(2)–N(7)–Rh(4) | 99.1(2)  |
| N(7)–C(4)  | 1.317(7) | N(1)–C(1)–N(2)   | 178.2(8) |
| N(8)–C(4)  | 1.156(7) | N(3)–C(2)–N(4)   | 176.8(7) |
|            |          | N(5)–C(3)–N(6)   | 175.8(8) |
|            |          | N(7)–C(4)–N(8)   | 179.0(6) |

Table 4  
Cyclic voltammetry data for the reduction and oxidation potentials of complexes **3**, **4a**, **4b**, **4c**, **5**, and **6**

| Compound  | $E_{1/2}$ vs. SCE (V)  | $i_{p,c}/i_{p,a}$ <sup>a</sup>           |
|---|--|--|
| [Cp*Ir(μ <sub>2</sub> -NCN- <i>N,N</i> )] <sub>2</sub> ( <b>3</b> )   | –1.38 <sup>b</sup><br>+0.99 <sup>c,d</sup><br>+1.38 <sup>c,d</sup>                         | 1.1<br>–<br>–                            |
| [Cp*Ir(μ <sub>3</sub> -NCN- <i>N,N,N'</i> ) <sub>3</sub> (IrCp*) <sub>3</sub> (μ <sub>3</sub> -NCN- <i>N,N,N</i> )] ( <b>4a</b> ) | +0.30 <sup>b</sup><br>+0.67 <sup>b</sup>   | 0.77<br>1.1                              |
| [Cp*Co(μ <sub>3</sub> -NCN- <i>N,N,N'</i> ) <sub>3</sub> (CoCp*) <sub>3</sub> (μ <sub>3</sub> -NCN- <i>N,N,N</i> )] ( <b>4b</b> ) | –0.79 <sup>b,e</sup><br>+0.11 <sup>c</sup><br>+0.68 <sup>c,d</sup><br>+0.91 <sup>c,d</sup> | –<br>1.0<br>–<br>–                       |
| [Cp*Rh(μ <sub>3</sub> -NCN- <i>N,N,N'</i> ) <sub>3</sub> (RhCp*) <sub>3</sub> (μ <sub>3</sub> -NCN- <i>N,N,N</i> )] ( <b>4c</b> ) | –1.25 <sup>b,e</sup><br>–0.99 <sup>b,e</sup><br>+0.29 <sup>c</sup><br>+0.92 <sup>c,d</sup> | –<br>–<br>0.81<br>–                      |
| [Cp*Ir(μ <sub>3</sub> -NCN- <i>N,N,N</i> )] <sub>4</sub> ( <b>5</b> )   | +0.65 <sup>c</sup><br>+1.08 <sup>c</sup><br>+1.18 <sup>c</sup>                             | 0.70<br>– <sup>f</sup><br>– <sup>f</sup> |
| Na[(Cp*Co) <sub>3</sub> (μ <sub>3</sub> -NCN- <i>N,N,N</i> ) <sub>2</sub> ] ( <b>6</b> )  | –1.13 <sup>b</sup><br>–0.19 <sup>c</sup><br>+0.59 <sup>c</sup>                             | 0.84<br>0.90<br>1.0                      |

<sup>a</sup> Peak currents ratio.

<sup>b</sup> Reduction potential.

<sup>c</sup> Oxidation potential.

<sup>d</sup> Irreversible peak observed only in the anodic process.

<sup>e</sup> Irreversible peak observed only in the cathodic process.

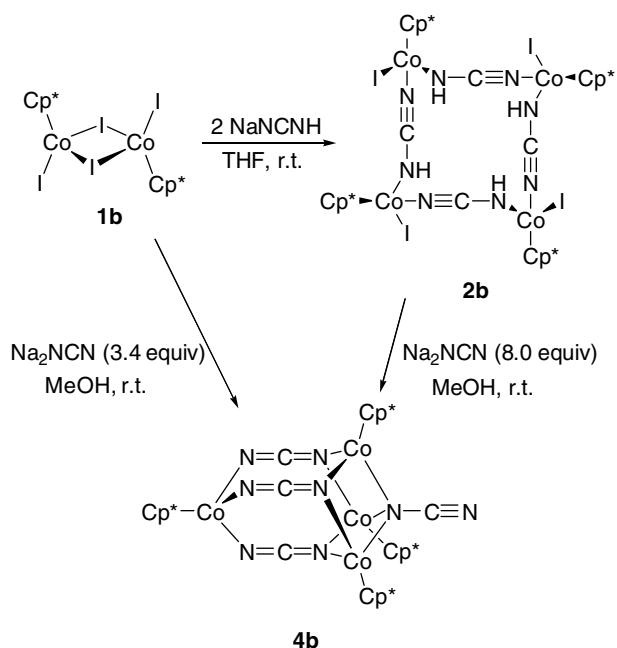
<sup>f</sup> Peak currents ratio cannot be calculated because two redox waves are overlapping.

## 3. Results and discussion

### 3.1. Synthesis of NCNH- and NCN-bridged Co(III)<sub>4</sub> complexes

When the Co(III) dimeric complex **1b** was treated in THF with 2 equiv of NaNCNH at room temperature, the NCNH-bridged tetracobalt complex **2b** was obtained in 55% yield (Scheme 2). Complex **2b** exhibits a pair of IR absorptions at 2203 and 1206 cm<sup>–1</sup> assignable to the asymmetric and symmetric stretching vibrations of the NCNH moiety, respectively, while the IR absorption at 3271 cm<sup>–1</sup> and the broad <sup>1</sup>H NMR signal at δ 3.58, the latter of which disappears on treatment with D<sub>2</sub>O, are assignable to the NH groups. Complex **2b** also shows one singlet at δ 1.49 due to the Cp\* protons. These spectra are fully comparable to those observed for the 16-membered macrocyclic NCNH-bridged tetrairidium complex **2a** (Table 5) and indicate that **2b** has a highly symmetrical structure composed of Cp\*CoI(NCNH) units.

The molecular structure of **2b** · CH<sub>2</sub>Cl<sub>2</sub> has been unambiguously determined by an X-ray analysis (Fig. 1). Complex **2b** has a characteristic 16-membered macrocyclic structure with an approximate *S*<sub>4</sub> symmetry, where each cobalt center adopts a three-legged piano-stool structure. The metric features of **2b** · CH<sub>2</sub>Cl<sub>2</sub> are closely related to those found for the iridium analogue [Cp\*IrI(μ<sub>2</sub>-NCNH-



Scheme 2. Transformation of NCNH- and NCN-bridged tetracobalt complexes.

$N,N'$ )] ·  $C_7H_8$  (**2a'** ·  $C_7H_8$ ) [**4a**]. The Co–N, N–C, C–NH, and NH–Co bond distances at 1.92, 1.14, 1.30, and 1.97 Å (mean values), respectively, as well as the Co–N–C, N–C–NH, and C–NH–Co bond angles at 169°, 173°, and 118° (mean values), respectively, suggest that the NCNH bridge is better described as a hydrogencyanamido(1–) ligand ( $N\equiv C-NH^-$ ) rather than a hydrogencyanobidimido(1–) ( $N=C=NH$ ), as has been confirmed for the structure of **2a'** ·  $C_7H_8$  (Table 2). The four cobalt atoms are arranged in a distorted tetrahedron, where the intramolecular distances between the NCNH-bridged Co atoms and between the diagonal Co atoms are *ca.* 5.59 and 6.20 Å (mean), respectively. It should be pointed out that examples of NCNH-bridged multinuclear complexes are still few in number [3,4a].

Switching the cyanamide source to react with complex **1b** from NaNCNH to  $Na_2NCN$  resulted in a change of the reaction product. Thus, treatment of **1b** with a small excess of  $Na_2NCN$  (3.4 equiv) in methanol at room temperature afforded the  $C_3$ -elongated cubane-like NCN-

bridged tetracobalt complex **4b**, instead of **2b**, in 48% yield. The  $^1H$  NMR signals at  $\delta$  1.39 (s) and 1.35 (s) with the intensity ratio of 1:3 assignable to the  $Cp^*$  protons, as well as a set of IR absorptions at 2068 (m) and 1997 (s)  $cm^{-1}$  assignable to the NCN asymmetrical stretching vibrations, are comparable to the analogous tetrairidium complex **4a** (Table 5) and suggest that complex **4b** consists of two distinct types of  $Cp^*Co$  and NCN units in the ratio of 1:3.

This reaction is in sharp contrast to that of **1a** with  $Na_2NCN$  which affords the NCN-bridged diiridium complex **3**, while the  $C_3$ -elongated cubane-like tetrairidium complex **4a** is synthesized *via* the reaction of the macrocyclic complex **2a** with  $NEt_3$ . In the case of cobalt, formation of dicobalt analogue of **3** could not be confirmed. In addition, complex **4b** was not obtained by treatment of **2b** with a weak base ( $NEt_3$ ). However, when an excess amount of  $Na_2NCN$  (8.0 equiv) was allowed to react with **2b** in methanol, complex **4b** was isolated in 37% yield. In the latter reaction,  $Na_2NCN$  behaves eventually as a strong base. We consider that the macrocyclic cobalt complex **2b** is of higher relative stability than the iridium analogue **2a**. It should also be noted that, unlike the iridium complex **4a** which can be thermally transformed into the regular cubane-type complex **5**, complex **4b** failed to undergo such skeletal rearrangement on heating in toluene or xylene.

### 3.2. Synthesis of NCNH- and NCN-bridged $Rh(III)_4$ complexes

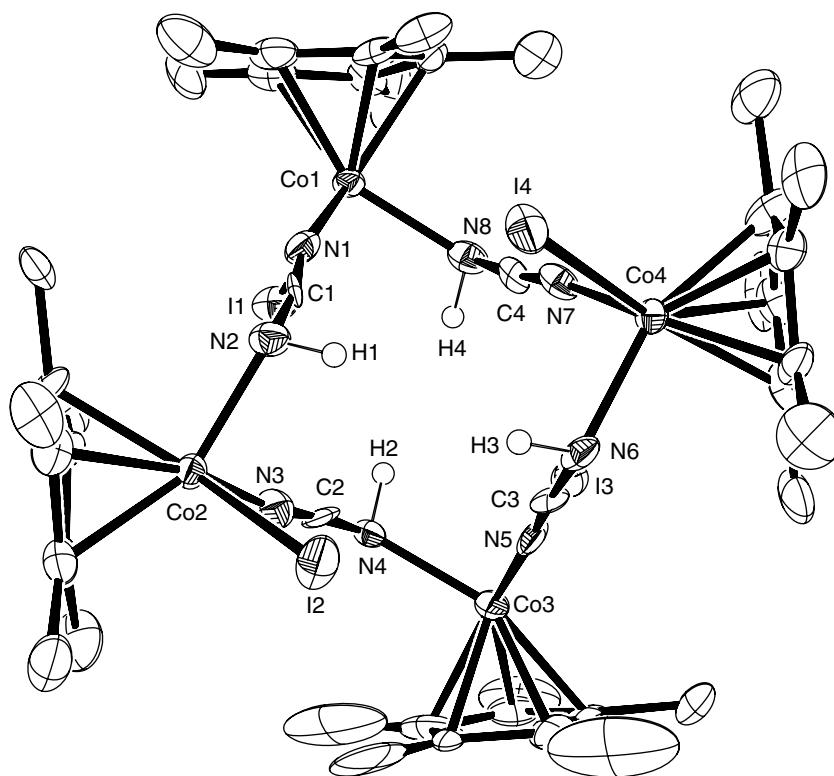
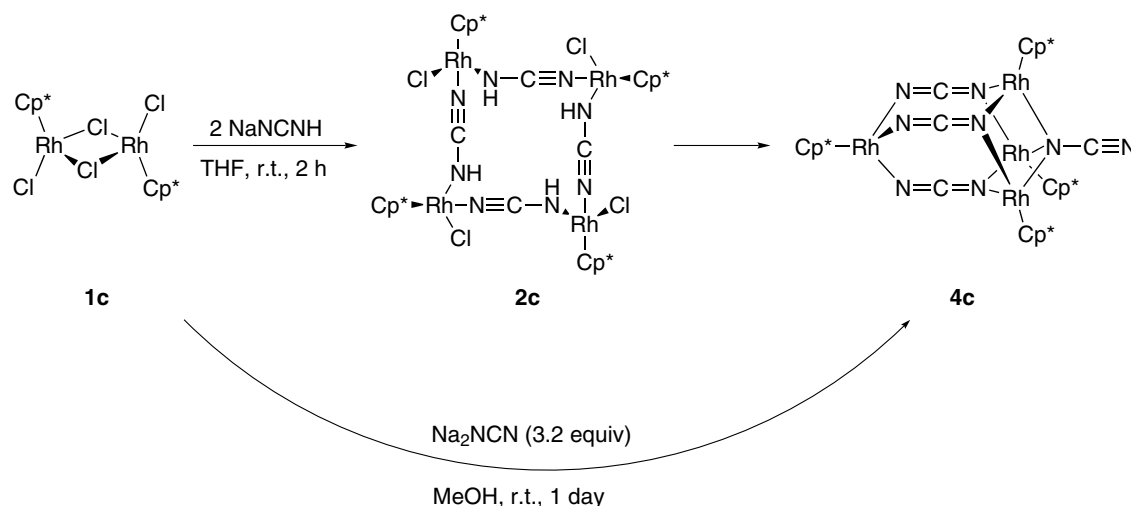
The  $Rh(III)$  complex **1c** was also found to be converted into similar NCN-bridged tetranuclear complexes. On treatment with 2 equiv of NaNCNH in THF at room temperature, formation of the macrocyclic tetrarhodium complex [ $Cp^*RhCl(\mu_2-NCNH-N,N')$ ]<sub>4</sub> (**2c**) was observed in a couple of hours. Complex **2c** exhibits  $^1H$  NMR signals at  $\delta$  4.26 (s) and 1.53 (s) assignable to the NH and  $Cp^*$  protons, while the IR absorptions at 3209 and 2188  $cm^{-1}$  are also comparable to the NCNH stretching vibrations of **2a–b** (Table 5). However, complex **2c** could not be isolated in a pure form, because **2c** gradually underwent further transformation to the  $C_3$ -elongated cubane-like tetrarhodium complex [ $Cp^*Rh(\mu_3-NCN-N,N,N')$ ]<sub>3</sub>( $RhCp^*$ )<sub>3</sub>( $\mu_3-NCN-N,N,N'$ ) (**4c**) under the above reaction conditions (Scheme 3).

Table 5  
NMR and IR spectra for complexes **2** and **4**

| Compound  | IR (KBr, $cm^{-1}$ ) <sup>b</sup> | $^1H$ NMR ( $C_6D_6$ , $\delta$ ) |
|---|-----------------------------------|-----------------------------------|
| [ $Cp^*IrCl(\mu_2-NCNH-N,N')$ ] <sub>4</sub> ( <b>2a</b> ) <sup>a</sup>   | 3221 (w), 2211 (s), 1215 (m)      | 3.57 (br, 4H), 1.55 (s, 60H)      |
| [ $Cp^*Ir(\mu_2-NCNH-N,N')$ ] <sub>4</sub> ( <b>2a')</b> <sup>a</sup>   | 3271 (w), 2218 (s), 1225 (m)      | 3.48 (br, 4H), 1.62 (s, 60H)      |
| [ $Cp^*CoI(\mu_2-NCNH-N,N')$ ] <sub>4</sub> ( <b>2b</b> )   | 3271 (w), 2203 (s), 1206 (m)      | 3.58 (br, 4H), 1.49 (s, 60H)      |
| [ $Cp^*RhCl(\mu_2-NCNH-N,N')$ ] <sub>4</sub> ( <b>2c</b> )  | 3209 (w), 2188 (s), 1204 (m)      | 4.26 (br, 4H), 1.53 (s, 60H)      |
| [ $Cp^*Ir(\mu_3-NCN-N,N,N')$ ] <sub>3</sub> ( $IrCp^*$ ) <sub>3</sub> ( $\mu_3-NCN-N,N,N'$ ) ( <b>4a</b> ) <sup>a</sup> | 2105 (m), 2043 (s), 1136 (m)      | 1.58 (s, 45H), 1.53 (s, 15H)      |
| [ $Cp^*Co(\mu_3-NCN-N,N,N')$ ] <sub>3</sub> ( $CoCp^*$ ) <sub>3</sub> ( $\mu_3-NCN-N,N,N'$ ) ( <b>4b</b> )              | 2068 (m), 1997 (s), 1154 (m)      | 1.39 (s, 15H), 1.35 (s, 45H)      |
| [ $Cp^*Rh(\mu_3-NCN-N,N,N')$ ] <sub>3</sub> ( $RhCp^*$ ) <sub>3</sub> ( $\mu_3-NCN-N,N,N'$ ) ( <b>4c</b> )              | 2054 (m), 2007 (s), 1146 (m)      | 1.57 (s, 45H), 1.55 (s, 15H)      |

<sup>a</sup> Ref. [4a], Supporting information.

<sup>b</sup> Only IR absorptions assignable to the NCNH or NCN stretching vibrations are shown.

Fig. 1. Molecular structure of **2b**. Ellipsoids at 50% probability.

Scheme 3. Transformation of NCNH- and NCN-bridged tetrahodium complexes.

Prolonged reaction (1 day) of **2c** with NaNCNH led to the formation of **4c** as the major product, but from a synthetic point of view, complex **4c** was cleanly obtained in high yield by the reaction of **1c** with a small excess amount of Na<sub>2</sub>NCN (3.2 equiv). The IR spectrum of **4c** shows a pair of absorptions at 2054 (m) and 2007 (s) cm<sup>-1</sup> due to the two types of NCN bridges, while the <sup>1</sup>H NMR spectrum shows a pair of Cp\* signals at δ 1.57 (s) and 1.55 (s) in the intensity ratio of 3:1. The detailed molecular structure of **4c** · 2C<sub>6</sub>H<sub>6</sub> has been determined by an X-ray

analysis (Table 3 and Fig. 2). The metric features of **4c** · 2C<sub>6</sub>H<sub>6</sub> are comparable to those found for **4a** · 0.5C<sub>6</sub>H<sub>6</sub> [4a]. The three NCN ligands (N–C, 1.192(7)–1.263(7) Å; N–C–N, 175.8(8)–178.2(8)°) lying in parallel with each other in the tetrahodium core adopt the carbodiimido(2-) structures (N<sup>-</sup>=C=N<sup>-</sup>) as the dominant canonical form and bridge the four rhodium centers with a μ<sub>3</sub>-κN,κN,κN' coordination mode, in which the Rh–N–C bond angles fall in the range of 119.0(5)–123.1(6)°. The fourth NCN ligand (N(7)–C(4)–N(8)) adopts the cyanamido(2-) structure

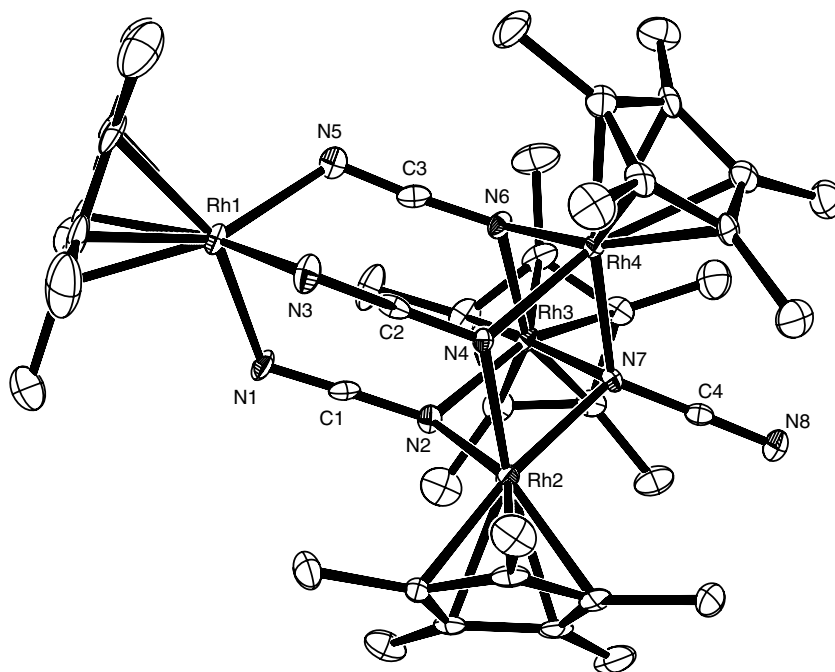


Fig. 2. Molecular structure of **4c**. Ellipsoids at 50% probability.

( $\text{N}\equiv\text{C}-\text{N}^{2-}$ ) as the dominant canonical form and caps the Rh(2), Rh(3), and Rh(4) centers with a  $\mu_3-\kappa\text{N},\kappa\text{N},\kappa\text{N}$  coordination mode. As a whole, the  $\text{Rh}_4(\text{NCN})_4$  core forms an elongated cubane-like skeleton with an approximate  $C_{3v}$  symmetry, one of the rhodium corners (Rh(1)) being separated by the three  $\mu_3-\text{NCN}-\text{N},\text{N},\text{N}'$  bridges. The intramolecular distances between Rh(1) and the other three Rh atoms are *ca.* 5.09 Å (mean), while the distances between these three Rh atoms are as short as 3.30 Å (mean). **4c** is also thermally stable like **4b** and failed to give the corresponding regular cubane-type complex on refluxing in *p*-xylene.

### 3.3. Electrochemical properties of the NCN-bridged Co(III), Rh(III), and Ir(III) complexes

Redox behaviors of the NCN-bridged group 9 metal complexes have been examined by cyclic voltammetry. Reduction and oxidation potentials of complexes **3–5** are

summarized in Table 4. The macrocyclic tetranuclear complexes **2a–c** are not stable under the cyclic voltammetry measurement conditions. For the tetranuclear Co and Rh complexes **4b** and **4c**, irreversible cathodic waves are observed below  $-0.7$  V (vs. SCE), while tetrairidium complexes **4a** and **5** shows no reduction down to  $-2.0$  V, and the diiridium complex **3** exhibits quasi-reversible cathodic wave at as low as  $-1.38$  V. On the other hand, quasi-reversible anodic waves have been observed for complexes **4a**, **4b**, **4c**, and **5** (Fig. 3). Interestingly, the first redox potentials shift positively in the order **4b** (Co) < **4c** (Rh) < **4a** (Ir), while only the iridium complex **4a** shows the second quasi-reversible redox process. Unfortunately, the oxidized species could not be isolated. For **5**, three single-electron anodic waves are observed. This redox behavior is compared with that of the related sulfido-bridged iridium cubane-type complex  $[\text{Cp}^*\text{IrS}]_4$ , which has been shown to undergo two-step single-electron oxidation to give the corresponding dication [17]. In these cases, the

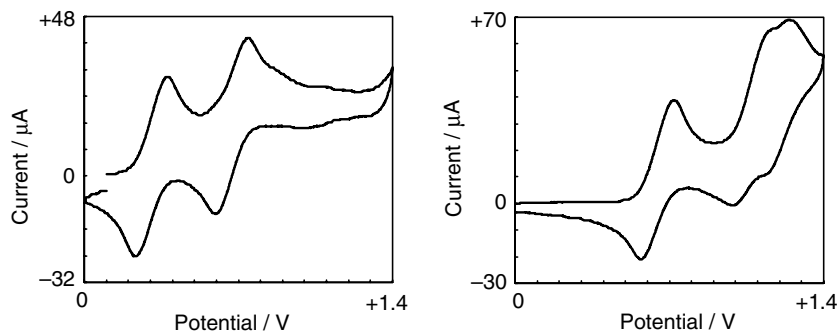


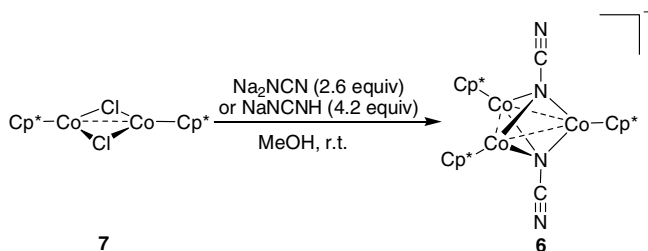
Fig. 3. Cyclic voltammograms for 2 mM **4a** (left) or **5** (right) in 0.1 M  $\text{NBu}_4^+\text{BF}_4^-/\text{CH}_2\text{Cl}_2$  at 25 °C with the scan ratio of 100 mV/s.

electron deficiency in the oxidized species is compensated by the formation of a metal–metal bond.

### 3.4. Synthesis and electrochemical property of the bis(NCN)-capped trinuclear Co(II) complex

Next, we have examined the assembly of Cp\*Co(II) fragments with NCN ligands. When the Co(II) dimeric complex **7** was treated with a small excess of Na<sub>2</sub>NCN (2.6 equiv) in methanol at room temperature, the anionic bis(NCN)-capped tricobalt complex **6** was obtained in 62% yield. The same product was also obtained in 49% yield by the reaction of **7** with an excess amount of NaNcNH (4.2 equiv) (Scheme 4).

Complex **6** shows IR absorptions at 2116 (s) and 1146 (m) cm<sup>-1</sup> assignable to the asymmetric and symmetric NCN stretching vibrations, respectively, while the <sup>1</sup>H NMR spectrum exhibits one broad signal at δ 20.52 assignable to the Cp\* protons, which strongly indicates that complex **6** is highly symmetrical as well as weakly paramagnetic (*g* = 2.05). Preliminary X-ray analysis of complex **6**, by which the positions of Na<sup>+</sup> and C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> could not be determined, supports the structure with a C<sub>3h</sub> symmetry, that is, the triangular Co<sub>3</sub> core are capped by two NCN ligands in a μ<sub>3</sub>-κN,κN,κN coordination mode [18]. The related bis(NCN)-capped trinuclear structures have been found in the cationic heterotrinuclear complexes [(Cp\*Ir)<sub>2</sub>(ML)(μ<sub>3</sub>-NCN-N,N,N)<sub>2</sub>]<sup>+</sup> (ML = RuCp, Rh(cod), and Pd(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)) [4b] and the anionic triruthenium(II) complex [(Cp\*Ru)<sub>3</sub>(μ<sub>3</sub>-NCN-N,N,N)<sub>2</sub>]<sup>-</sup> [19].



Scheme 4. Synthesis of the anionic bis(NCN)-capped tricobalt complex.

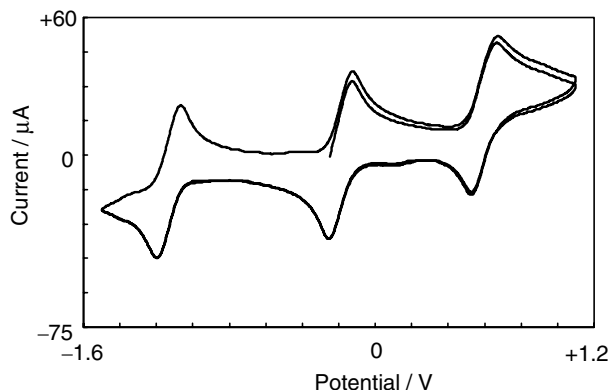


Fig. 4. Cyclic voltammogram for 2 mM **6** in 0.1 M NBu<sub>4</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup>/CH<sub>2</sub>Cl<sub>2</sub> at 25 °C with the scan ratio of 100 mV/s.

The redox behavior of **6** has also been examined by cyclic voltammetry (Table 4). As depicted in Fig. 4, two single-electron quasi-reversible anodic waves (−0.19, +0.59 V) and one single-electron quasi-reversible cathodic wave (−1.13 V vs. SCE) have been confirmed, which reveal the electron-rich nature of the anionic tricobalt complex. Obviously these waves correspond to the redox processes between the Co(I)Co(II)<sub>2</sub>, Co(II)<sub>3</sub>, Co(II)<sub>2</sub>Co(III), and Co(II)Co(III)<sub>2</sub> species.

## 4. Conclusions

The 16-membered macrocyclic NCNH-bridged tetracobalt(III) complex **2b**, the C<sub>3</sub>-elongated cubane-like NCN-bridged tetracobalt(III) and tetrarhodium(III) complexes **4b** and **4c**, and the anionic bis(NCN)-capped tricobalt(II) complex **6** have newly been synthesized. The choice of the cyanamide source (Na<sub>2</sub>NCN, NaNcNH) plays a critical role in some cases. Electrochemical studies of **4a–c**, **5**, and **6** have revealed that **4** and **5** have one or more quasi-reversible oxidations, while **6** undergoes one quasi-reversible reduction and two quasi-reversible oxidation processes. Further studies on the reactivities of these homometallic group 9 complexes are now under investigation.

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## Appendix A. Supplementary data

Crystallographic data for the structural analyses in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 299666 and 299667 for compounds **2b** · CH<sub>2</sub>Cl<sub>2</sub> and **4c** · 2C<sub>6</sub>H<sub>6</sub>, respectively. Copies of the data are available free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1123 336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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