

# Supplementary Materials: On the Aqueous Solution Behavior of C-Substituted 3,1,2-Ruthenadecarbadodecaboranes

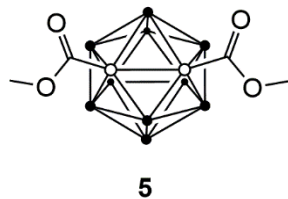
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## 1. Synthesis of 5 and 6

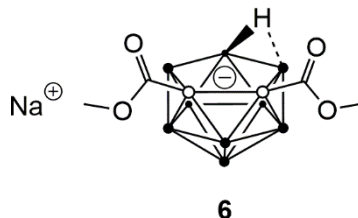
### 1,2-(CO<sub>2</sub>Me)<sub>2</sub>-*closo*-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (5)



1,2-(CO<sub>2</sub>Me)-*closo*-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub> (5) was synthesized according to a modified literature procedure [1].

*ortho*-Carborane (2.00 g, 13.9 mmol, 1.0 eq.) was dissolved in 25 mL toluene/Et<sub>2</sub>O 2:1 (v/v) under nitrogen atmosphere, then cooled to −78 °C. An *n*-BuLi solution (1.57 M sol. in *n*-hexane, 18.6 mL, 28.5 mmol, 2.05 eq.) was added dropwise, and the mixture was stirred and left to warm-up to room temperature over one hour. After stirring for 2.5 hours at room temperature, the reaction mixture was cooled to 0 °C and chloroformate (30.58 mmol, 2.88 g, 2.35 mL, 2.2. eq.) was added in one portion. The mixture was then brought to reflux for 17 h, after which the reaction was quenched with 10 mL H<sub>2</sub>O. The organic phase was diluted with 50 mL Et<sub>2</sub>O, the combined organic phases dried over MgSO<sub>4</sub> and evaporated to dryness, yielding pure 5 as a colorless powder. <sup>1</sup>H and <sup>11</sup>B NMR data (CDCl<sub>3</sub>) were in accordance to those reported in the literature [1].

### Sodium 7,8-(CO<sub>2</sub>Me)<sub>2</sub>-*nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub> (6)



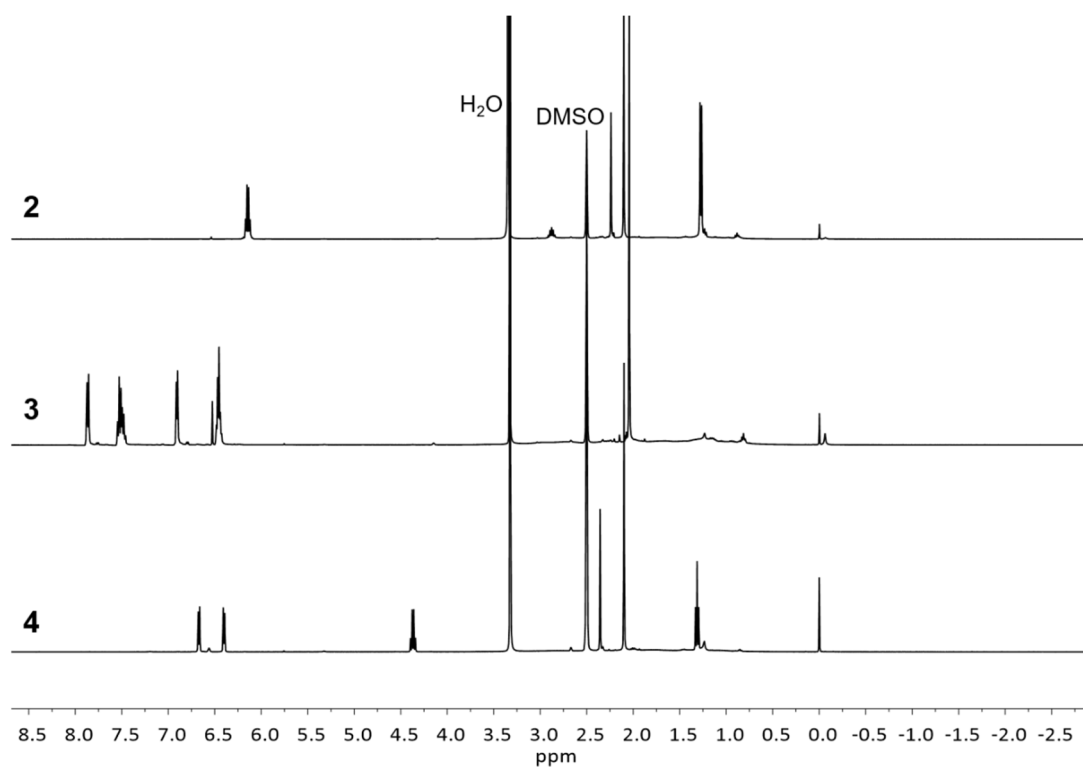
5 (0.172 g, 0.85 mmol, 1.0 eq.) was dissolved in 30 mL degassed MeCN/H<sub>2</sub>O 2:1 (v/v) under nitrogen atmosphere, and stirred at room temperature for two hours, during which gas evolution (H<sub>2</sub>) was observed. Reaction progress was monitored via TLC (ethyl acetate). Amberlite (IR120, Na<sup>+</sup>) was added, and the mixture was stirred for 1.5 hours. The reaction mixture was then filtered, and the solvent was evaporated *in vacuo*, using a cooling trap. The white residue was stirred overnight with dry *n*-hexane, filtered and dried *in vacuo* (50 °C, 10<sup>−3</sup> mbar), to yield 91.0 mg (50%) of pure 6. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ (ppm) = −2.59 (br s, 1H, *endo-H*) (*endo-H* is the „extra“ hydrogen on top of the C<sub>2</sub>B<sub>3</sub> face of the *nido*-carborate(−1) anion), −0.41–2.95 (br, B–H), 3.52 (s, 6H, OCH<sub>3</sub>). <sup>11</sup>B NMR (CD<sub>3</sub>CN): δ (ppm) = −8.4 (d, 2B, <sup>1</sup>J<sub>BH</sub> = 142 Hz), −11.7 (d, 1B, <sup>1</sup>J<sub>BH</sub> = 168 Hz), −16.2 (d, 2B, <sup>1</sup>J<sub>BH</sub> = 139 Hz), −20.9 (d, 2B, <sup>1</sup>J<sub>BH</sub> = 156 Hz), −32.3 (dd, 1B, <sup>1</sup>J<sub>BH</sub> = 141, 30 Hz, B(10)), −35.3 (d, 1B, <sup>1</sup>J<sub>BH</sub> = 143 Hz).

## 2. Crystallographic Data for 4 and 7

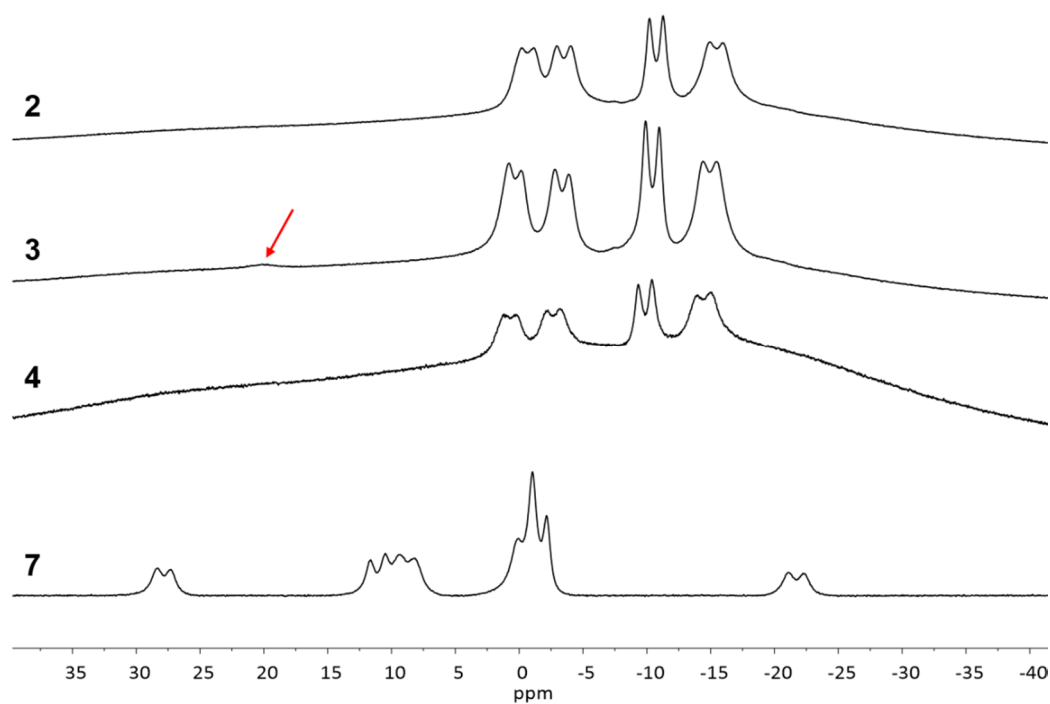
**Table S1.** Crystal data for 4 and 7.

	4	7
Empirical formula	C <sub>14</sub> H <sub>27</sub> B <sub>9</sub> O <sub>2</sub> Ru	C <sub>16</sub> H <sub>29</sub> B <sub>9</sub> O <sub>4</sub> Ru
Formula weight	425.71 g mol <sup>-1</sup>	483.75 g mol <sup>-1</sup>
<b>Data collection</b>		
Reflections collected	15878	39554
Independent reflections	4452 ( <i>R</i> <sub>int</sub> = 0.0487)	7468 ( <i>R</i> <sub>int</sub> = 0.0369)
Θ <sub>max</sub>	28.282°	32.492°
Completeness (%)	93.3	94.4
Crystal system	Monoclinic	Triclinic
Unit cell	<i>a</i> = 7.9939(3) Å	<i>a</i> = 9.3310(2) Å
	<i>b</i> = 26.816(1) Å	<i>b</i> = 9.4169(2) Å
	<i>c</i> = 9.1272(3) Å	<i>c</i> = 14.0477(3) Å
	β = 100.926(3)°	α = 90.693(2)° β = 103.321(2)° γ = 113.757(2)°
Volume	1921.1(1) Å <sup>3</sup>	1091.71(4) Å <sup>3</sup>
Space group	<i>P</i> 2 <sub>1</sub> /c	<i>P</i> $\bar{1}$
<i>Z</i>	4	2
ρ <sub>calc</sub>	1.472 Mg m <sup>-3</sup>	1.472 Mg m <sup>-3</sup>
μ(Mo-Kα)	0.821 mm <sup>-1</sup>	0.739 mm <sup>-1</sup>
<b>Refinement</b>		
Data/restraints/parameters	4452/0/239	7468/0/276
<i>R</i> ( <i>I</i> > 2σ <i>I</i> )	0.0502	0.0257
<i>R</i> <sub>w</sub> ( <i>I</i> > 2σ <i>I</i> )	0.0766	0.0581
<i>R</i> (all data)	0.0671	0.0311
<i>R</i> <sub>w</sub> (all data)	0.0807	0.0603
Max. / Min. residual electron density	0.574 / −0.658 e·Å <sup>-3</sup>	0.688 / −0.667 e·Å <sup>-3</sup>
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.201	1.063

### 3. NMR Spectra



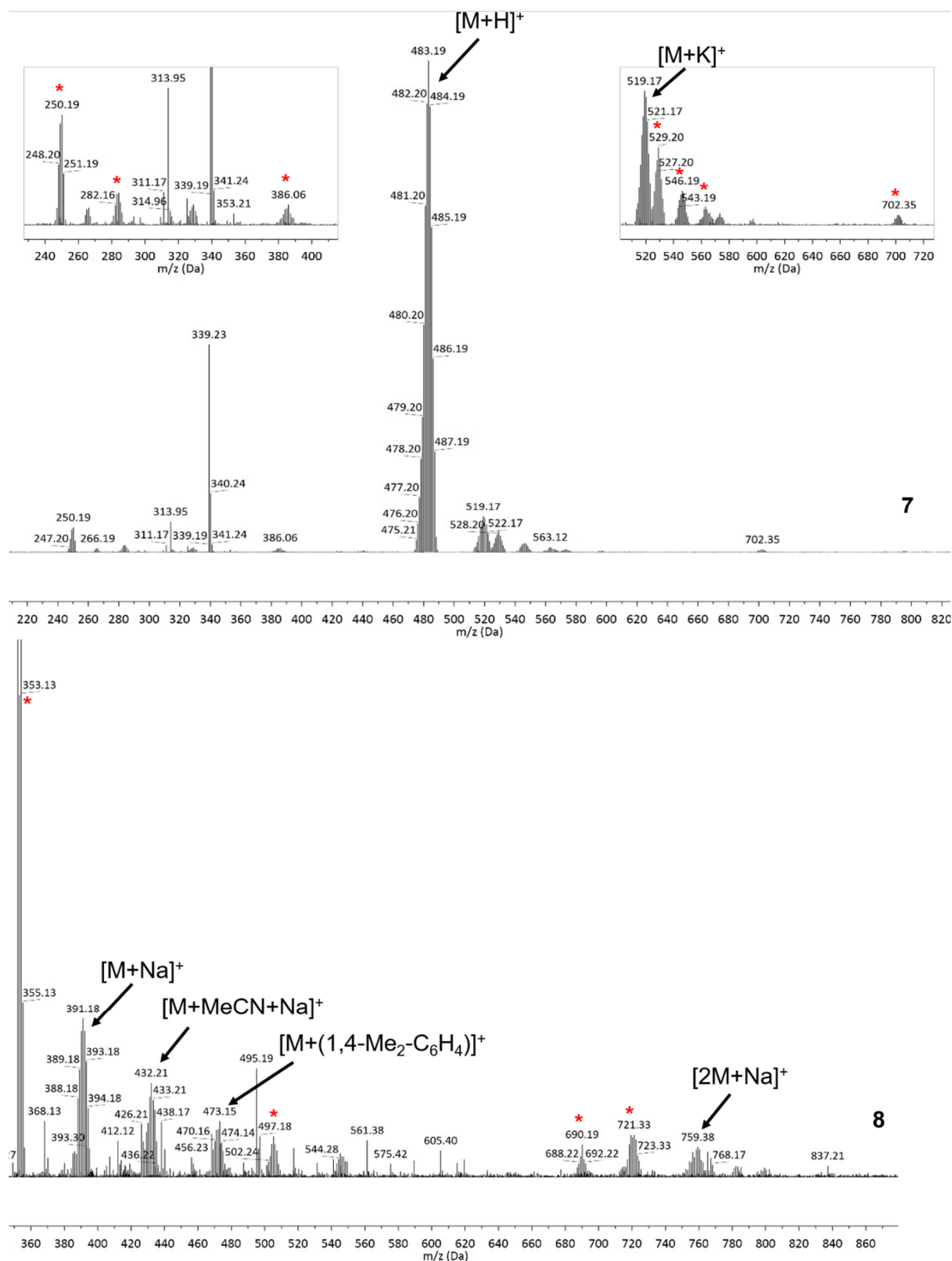
**Figure S1.**  $^1\text{H}$  NMR spectra (400.13 MHz) of complexes **2–4** in wet  $\text{DMSO-d}_6$  in air at room temperature, after one month. No signals corresponding to the uncoordinated ligands (i.e. arene and *nido*-carborate(−1)) were found.



**Figure S2.**  $^{11}\text{B}$  NMR spectra (128.83 MHz) of complexes **2–4** and **7** in wet  $\text{DMSO-d}_6$  in air at room temperature, after one month. Red arrow indicates the small broad signal in the  $^{11}\text{B}$  NMR spectrum of **3**, probably due to the presence of aggregates of **3** in  $\text{DMSO-d}_6$  solution. No signals for uncoordinated *nido*-carborate(−1) ligand were found for all studied complexes.



#### 4. ESI-MS(+) Spectra of 7 and 8 in MeCN/H<sub>2</sub>O Mixtures



**Figure S3.** ESI(+) mass spectra of 7 (top) and 8 (bottom) measured in MeCN/H<sub>2</sub>O (98:2, v/v). The peaks which could not be unequivocally assigned are indicated by \*. The insets for 7 show a section of the region  $m/z$  = 240–400 (top left) and 520–720 (top right).

## 5. Nanoparticle Tracking Analysis (NTA)

**Table S2.** Mean size and concentration of particles for PBS/DMSO solutions of **2**, **7** and **8**.

Solution	Concentration (particles mL <sup>-1</sup> ) <sup>a</sup>	Size (nm) <sup>a</sup>
<b>2</b>	$1.59 \times 10^9 \pm 8.90 \times 10^7$	$156.3 \pm 2.4$
<b>7</b>	$1.02 \times 10^8 \pm 1.48 \times 10^7$	$155.2 \pm 12.7$
<b>8</b>	$6.15 \times 10^8 \pm 1.67 \times 10^7$	$190.6 \pm 6.8$

<sup>a</sup> Averaged mean from five independent captures.

## 6. References

1. Fein, M.M.; Grafstein, D.; Paustian, J.E.; Bobinski, J.; Lichstein, B.M.; Mayes, N.; Schwartz, N.N.; Cohen, M.S. Carboranes. II. The Preparation of 1- and 1,2-Substituted Carboranes. *Inorg. Chem.* **1963**, *2*, 1115–1119.