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# Space Craft-like Octanuclear Co(II)-Silsesquioxane Nanocages: Synthesis, Structure, Magnetic Properties, Solution Behavior, and Catalytic Activity for Hydroboration of Ketones

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#### Supporting Information

ABSTRACT: Two novel space craft-like octanuclear Co(II)-silsesquioxane nanocages,  $\{\operatorname{Co}_8[(\operatorname{MeSiO}_2)_4]_2(\operatorname{dmpz})_8\}$  (SD/Co8a) and  $\{\operatorname{Co}_8[(\operatorname{PhSiO}_2)_4]_2(\operatorname{dmpz})_8\}$  (SD/Co8b) (SD = SunDi; Hdmpz = 3,5-dimethylpyrazole), have been constructed from two similar multidentate silsesquioxane ligands assisted with a pyrazole ligand. The  $Co_8$  skeleton consists of eight tetrahedral Co(II) ions arranged in a ring and is further capped by two  $(MeSiO_2)_4$  ligands up and down. The auxiliary dmpz- ligands seal the ring finally. Electrospray ionization mass spectrometry revealed SD/Co8a and SD/Co8b are highly stable in CH<sub>2</sub>Cl<sub>2</sub>. Magnetic analysis implies that SD/Co8a announces antiferromagnetic interactions between Co(II) ions. Moreover, both of them display good homogeneous catalytic activity for hydroboration of ketones in the presence of pinacolborane under mild conditions.



# ■ INTRODUCTION

The ongoing research interest in polynuclear metal-organic nanocages (MONCs) is motivated by their fascinating structures and miscellaneous applications, including catalysts, sensors,<sup>2</sup> and molecular magnets.<sup>3</sup> Up to now, numerous MONCs have been springing up and exhibit diverse structures, which pours new energy into the modern coordination chemistry field.<sup>4</sup> As we know, the rational selection of multidentate ligands of special geometry bearing suitable coordination sites to "capture" or "ligate" multiple metal ions is extremely crucial to fabricate MONCs.<sup>5</sup> From small M<sub>6</sub>L<sub>12</sub> octahedra, M<sub>12</sub>L<sub>24</sub> cuboctahedra, M<sub>24</sub>L<sub>48</sub> rhombicuboctahedra, to the currently largest M<sub>30</sub>L<sub>60</sub> icosidodecahedron reported by the Fujita group, the special ligand effect in the construction of MONCs is fully demonstrated.<sup>5e-h</sup> Given this, silsesquioxane  $[RSiO_{1.5}]_n$  with varied oligometric forms, preorganized multiple O coordination sites, high coordination flexibility and reactivity can be the next-generation macrocyclic ligands used to construct MONCs with increased stability due to cooperativity between the binding sites, but such kinds of ligands have been

rarely studied to date.<sup>6–13</sup> Generally, precursor  $\{R_1Si(OR_2)_3\}$ is actually metastable in alkaline solution and can transform into various oligomeric  $[RSiO_{1.5}]_n$  (n = 1, 2, 4, 5, 6, 7, 8, 9, 10, 12) intermediates.<sup>6-13</sup> Thus, it is conceivable that using in situ hydrolysis of  $\{R_1Si(OR_2)_3\}$  to generate multidentate cyclic or acyclic silsesquioxane ligands is a promising strategy to construct a diverse range of MONCs with interesting properties. Indeed, as the literature has documented, sporadic silsesquioxane-based MONCs containing Cu(II),<sup>7</sup> Fe(III),<sup>8</sup> Ni(II),<sup>9</sup> Co(II),<sup>10</sup> Cd(II),<sup>11</sup> and bimetal<sup>12</sup> have been isolated. For example, the  $\{Cu_{24}\}$  MONC with charming geometry and good catalytic activity has been reported as the highestnuclearity silsesquioxane-based Cu(II) MONC until now.7a Another hexanuclear Fe(III) MONC incorporating two kinds of different silsesquioxanes with interesting magnetic properties was also reported.<sup>8a</sup> Normally, cobalt complexes are much more attractive due to their variable valences (+2 and +3) and

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the flexible coordination geometries (4-coordinated tetrahedron and 6-coordinated octahedron), which endow them fascinating magnetism and catalytic activity. However, Co(II)-silsesquioxane cages are relatively rare and develop slowly among various metal-silsesquioxane MONCs. Currently the highest-nuclearity Co(II)-silsesquioxane MONC is a  $\{Co_6\}$  until now.<sup>10a</sup>

On the basis of these considerations and our previous work in transitional metal clusters,<sup>14</sup> we successfully isolated two highest-nuclearity  $\{Co_8\}$  cages in the Co(II)-silsesquioxane MONCs family (Scheme 1), namely,  $\{Co_8[(MeSiO_2)_4]_2$ -

Scheme 1. Synthetic Routes for SD/Co8a and SD/Co8b<sup>a</sup>



<sup>a</sup>The photos are the crystals of **SD/Co8a** and **SD/Co8b** taken by a digital camera under the microscope.

 $(dmpz)_8$  (SD/Co8a), and  $\{Co_8[(PhSiO_2)_4]_2(dmpz)_8\}$  (SD/Co8b) (Hdmpz = 3,5-dimethylpyrazole). Both of them present similar space craft-like cage structures containing an equatorial ring of eight Co atoms which are capped by two (RSiO\_2)\_4 silsesquioxanes up and down and then sealed by eight dmpz<sup>-</sup> ligands near the equator region. The  $\{(RSiO_2)_4\}$  ligand exhibits a 4-fold symmetry with four lower-rim O atoms dangling for reinforcing the internal  $\{Co_8\}$  core. Their structures, solution stabilities, magnetic properties, and the catalytic activities have been studied in detail.

#### RESULTS AND DISCUSSION

Syntheses of SD/Co8a and SD/Co8b. The syntheses of Co(II)-methylsilsesquioxane nanocages need a two-step fashion. In the first step, in situ hydrolysis of methyltrialkoxysilane {MeSi(OMe)<sub>3</sub>} in the presence of NaOH in alcohol can produce a mixture of oligomeric siloxanolate [(MeSi(O)- $ONa)_n$  intermediates. In the second step, the intermediate siloxanolate  $[(MeSi(O)ONa)_n]$  was reacted with  $Co(NO_3)_2$ . 6H<sub>2</sub>O and auxiliary dmpz<sup>-</sup> ligand in DMF/MeCN solution under the solvothermal condition. After standing the reaction solution for 2-3 days at room temperature, blue cubic crystals of SD/Co8a were formed (yield: 50% based on  $Co(NO_3)_2$ .  $6H_2O$ ). The octanuclear Co(II)-silsesquioxane structure of SD/Co8a was confirmed by single crystal X-ray analysis. By switching silsesquioxanes from {MeSi(OMe)<sub>3</sub>} to {PhSi- $(OMe)_3$  a similar structure, SD/Co8b, can also be isolated by a similar method (yield: 60% based on  $Co(NO_3)_2 \cdot 6H_2O$ ). The bulk samples were collected as the crystals (Figure S1).

It is noted that siloxanolates are inclined to transform into various intermediate  $[RSiO_{1.5}]_n$  (n = 1, 2, 4, 5, 6, 7, 8, 9, 10, 12)<sup>6–13</sup> structures in the first step. However, the tetrameric silsesquioxane was only observed in di- and tetranuclear Ti(IV) MONCs previously.<sup>15</sup> In this work, we obtained two highest

nuclearity Co(II)-silsesquioxane MONCs based on tetrameric silsesquioxanes.

**Crystal Structures of SD/Co8a and SD/Co8b.** The SD/ **Co8a** and **SD/Co8b** crystallize in the monoclinic  $P2_1/n$  and orthorhombic *Pbcn* space groups, respectively (Table S1). The asymmetric units of **SD/Co8a** and **SD/Co8b** consist of a complete and one-half of the molecules, respectively. They exhibit similar space craft-like nanocage structures protected by outer silsesquioxanes and auxiliary dmpz<sup>-</sup> ligands (Figure 1a–



Figure 1. (a, b) Total structures of SD/Co8a and SD/Co8b; (c, d) the space craft-like skeleton of octanuclear Co(II)-silsesquioxane nanocage; (e) the crown-like  $\{Co_8O_8\}$  core; (f) the tetrameric  $[RSiO_2]_4$  ligands in SD/Co8a and SD/Co8b. Color code: Co, cyan; Si, yellow; O, red; C, gray; N, blue.

d). Both of them are in an approximate  $C_4$  symmetry. As shown in Figure 1a,b, both compounds comprise eight Co atoms, two silsesquioxane ligands, and four dmpz<sup>-</sup> ligands. On the basis of bond-valence sum (BVS) analysis,<sup>16</sup> all Co ions are in the +2 oxidation state (Table S4 and Table S5). Eight Co(II) ions are coplanar (Figure 1c) and arranged in an eightmembered ring connected by eight O atoms to form a  ${Co_8O_8}$  crown (Figure 1e). The Co-Co separations are in the range of 3.13-3.18 and 3.11-3.18 Å for SD/Co8a and SD/Co8b, respectively. Eight  $\mu_2$ -dmpz<sup>-</sup> ligands seal the Co<sub>8</sub> cage near the equator region. Eight dmpz ligands are distributed evenly up and down the plane of Co<sub>8</sub> ring. Eight Co(II) ions exhibit the same four-coordinated tetrahedral geometry by coordinating two O atoms from two silsesquioxane ligands and two N atoms from two dmpz<sup>-</sup> ligands. The Co-O, Co-N bond lengths and O-Co-O, N-Co-N, O-Co-N bond angles (Table S2 and Table S3) are all located in the normal range of Co(II) compounds.<sup>17</sup> Two silsesquioxane ligands also present the same coordination mode by bearing four terminal  $\mu_2$ -O atoms to bridge eight Co(II) ions to give a  $\{Co_8O_8\}$  crown (Figure 1e). Two  $[RSiO_2]_4$  ligands up and

down the plane of the  $Co_8$  ring are staggered with the rotation angle of 45.7 and 45.1° for **SD/Co8a** and **SD/Co8b**, respectively (Figure S2). It is worthy to note that the planar { $Co_8$ } core and the cyclic tetrasiloxide ligand are very rare in Co clusters and metallasiloxanes fields, respectively.

Electrospray Ionization Mass Spectrometry (ESI-MS). Recently, the ESI-MS technique was used more and more in coordination chemistry to detect the solution behaviors and solution assembly mechanism.<sup>18</sup> In order to investigate the stabilities of SD/Co8a and SD/Co8b in solvents, ESI-MS of them dissolved in dichloromethane were measured in a positive-ion mode. As depicted in Figure 2a,b, both SD/



Figure 2. Positive-ion ESI-MS of SD/Co8a (a) and SD/Co8b (b) dissolved in dichloromethane. The experimental (black line) and simulated (red line) isotope distributions of 1a to 1d and 2a to 2b.

**Co8a** and **SD/Co8b** display four identifiable species with the charge state of +1 in the ranges of m/z = 1800-1950 and 2300-2450 for **SD/Co8a** and **SD/Co8b**, respectively. The predominant species (**1d** and **2b**), centered at m/z = 1929.9524 and 2351.9749, can be assigned to [**SD/Co8a** + dmpz + 2H]<sup>+</sup> (calcd m/z = 1929.9381) and [**SD/Co8b** + Na]<sup>+</sup> (calcd m/z = 2351.9913), respectively. The parent peaks of **SD/Co8a** were observed as **1a** and **1b**, ascribed to [**SD/Co8a** + H]<sup>+</sup> (calcd m/z = 1832.8676) and [**SD/Co8a** + Na]<sup>+</sup> (calcd m/z = 1855.8685). The details of assigned formulas for **1a**-1d and **2a**-2d are listed in Table S6. On the basis of these formulas, we found all labeled peaks have the {Co<sub>8</sub>} skeleton, which means **SD/Co8a** and **SD/Co8b** retain their structural integrity in dichloromethane.

**Magnetic Properties.** Magnetic properties were investigated on **SD/Co8a** using a Quantum Design MPMS XL-5 magnetometer. Susceptibility has been measured between 2 and 300 K in a constant magnetic field of 1 kOe, and the magnetization was measured between -50 kOe and 50 kOe at a constant temperature of 2 K. The data presented in Figure 3 were corrected for the temperature-independent contribution of core electrons as obtained from Pascal's tables.<sup>19a</sup>



**Figure 3.** (a) Temperature-dependent susceptibility  $\chi(T)$  of **SD**/**Co8a**. The red (dashed) and the green (full) line are the best fits with eqs 1 and 2, respectively. Inset shows the same  $\chi(T)$  in an expanded scale around the maximum of the susceptibility. (b) Isothermal magnetization at 2 K and effective magnetic moment measured in a magnetic field of 1 kOe (inset).

The susceptibility of **SD/Co8a**  $\chi = M/H$  measured in a magnetic field of 1 kOe (Figure 3a) monotonically increases from  $\chi = 0.062$  emu/mol at 300 K to a local maximum of 0.256 emu/mol at 9.4 K (see inset in Figure 3a). From the room temperature susceptibility, an effective magnetic moment  $\mu_{eff}$  per cobalt ion can be calculated as  $\mu_{eff} = 2.828 \sqrt{\chi T/8}$ ,<sup>19b</sup> where the factor 8 in the denominator is due to the 8 cobalt ions per formula unit. The obtained value  $\mu_{eff(T=300 \text{ K})} = 4.3 \,\mu_{\text{B}}$  is slightly higher than the theoretically expected value for Co(II) ions with no orbital contribution (L = 0) which amounts to 3.87  $\mu_{\text{B}}$ .<sup>19c</sup> However, the measured effective magnetic moment of 4.3  $\mu_{\text{B}}$  is in a range of usually measured values for Co(II) ions with a quantum number of total electronic spin angular momentum S = 3/2 and a small but nonzero quantum number of total orbital angular momentum L.<sup>19c</sup>

The maximum at 9.4 K is a clear indication of an antiferromagnetic interaction between the Co(II) ions in a molecule. The same conclusion can be made observing the temperature dependence of effective magnetic moment per

Co(II) ion (inset in Figure 3b). It decreases from the already mentioned room temperature value of 4.3  $\mu_{\rm B}$  down to 0.8  $\mu_{\rm B}$  at 2 K.

Below 5 K the susceptibility starts to increase again with decreasing temperature. This so-called "Curie tail" can be attributed to a minute concentration of localized, non-interacting spin in the sample.

Figure 3b shows an isothermal magnetization M(H)measured at 2 K. A small value of the magnetization (at 50 kOe it is only ~0.2  $\mu_{\rm B}$  per Co(II) ion, while in saturation one can expect approximately  $g \cdot S \cdot \mu_B \approx 3 \mu_B$  per Co(II) ion) and linear dependence of M vs H at the beginning are again the confirmation of the antiferromagnetic ordering of magnetic moments in a molecule. At the magnetic field H of approximately 40 kOe, the M(H) curve starts to increase more rapidly (the increase of a derivative dM/dH can be observed). At this magnetic field, the interaction energy between the individual Co(II) magnetic moment and the external magnetic field becomes comparable with the energy due to the antiferromagnetic exchange coupling between Co(II) magnetic moments. The external magnetic field starts to rotate magnetic moments more efficiently in the direction of the external magnetic field.

According to the structure of **SD**/**Co8a**, a considerable magnetic interaction can be expected only between eight intramolecular Co(II) ions. They built a circle, each Co(II) bridged with two neighbors with the two bridges: Co-O-Co and Co-N-N-Co. As the distances between all nearest neighbor Co(II) ions and the bond angles between them are similar, the same exchange interaction parameter J between them can be proposed.

As the first approximation to estimate the interaction parameter *J* a circle of eight Co(II) S = 3/2 ions is considered as an "infinite" chain of classical vectors with interaction Hamiltonian between two neighbors  $\mathcal{H}_{int} = -2 J \Sigma S_1 S_2$ . In this case, the temperature-dependent susceptibility can be described with the following eq 1:

$$\chi = 8 \frac{Ng^2 \mu_B^2 S(S+1)}{3k_B T} \frac{1+u}{1-u}$$
(1)

$$u = \operatorname{coth}\left[\frac{2JS(S+1)}{k_{\rm B}T}\right] - \left[\frac{k_{\rm B}T}{2JS(S+1)}\right]$$

The prefactor 8 is used due to eight cobalt ions in a formula unit. Other symbols acquire their usual meanings. The spin S was set to S = 3/2, while the interaction parameter J and gfactor were left as free parameters during the fitting procedure. The best correspondence between eq 1 and the measured data for T > 6 K (below 6 K the prevailing signal is the "Curie tail" due to uncoupled magnetic ions for which eq 1 is not applicable) was obtained with  $J/k_{\rm B} = -10.9 \text{ K} (-7.6 \text{ cm}^{-1})$ and g = 2.2 (see the red dashed line in Figure 3a). A rather large difference between the model and the measured data is mainly because eq 1 does not take into account the single ion effects, like spin-orbit coupling-we have shown the quantum number of total orbital angular momentum L is not zero—and a crystal field effect. For the theoretical description of a system of eight interacting cobalt ions the Hamiltonian:  $\mathcal{H} = \mathcal{H}_{int} +$  $\mathcal{H}_{\rm SO}$  +  $\mathcal{H}_{\rm CF}$  +  $\mathcal{H}_{\rm Z}$ , where  $\mathcal{H}_{\rm int}$  takes account of the interaction,  $\mathcal{H}_{SO}$  spin–orbit coupling,  $\mathcal{H}_{CF}$  crystal field, and  $\mathcal{H}_z$  is the Zeeman term, should be constructed. The solving of such a Hamiltonian is highly demanding numerical task, and enough computer power should be available.

In order to estimate the interaction parameter J and considering at least phenomenologically also the single ion effects,  $\chi(T)$  was analyzed using Rueff's approach using eq 2:

$$\chi = \frac{A \exp\left(-\frac{E_1}{k_{\rm B}T}\right) + B \exp\left(-\frac{E_2}{k_{\rm B}T}\right)}{T}$$
(2)

where A + B is the Curie constant, and  $E_1$  and  $E_2$  represent the activation energies corresponding to the single ion effects, and the antiferromagnetic interaction parameter J. The excellent agreement between the experimental data for T > 6 K and eq 2 is shown as a full green line in Figure 3a with parameters A + B= 21.8 emu K/mol (from which follows g = 2.4),  $E_1/k_B = 52$  K, and  $E_2/k_B = 8.2$  K. The obtained g-factor and the single ion effects are on the order of values found in the literature.<sup>19d,e</sup> The activation energy  $E_1/k_{\rm B}$ , corresponding to the interaction parameter  $J = -2E_1/k_B = -16 \text{ K} (-11.1 \text{ cm}^{-1})$  is a bit larger as the one when cobalt magnetic moments were treated as classical vectors  $(J/k_{\rm B} \text{ of } -11.1 \text{ cm}^{-1} \text{ versus } -7.6 \text{ cm}^{-1})$ . We can conclude that the maximum in the measured susceptibility at 9.4 K can be attributed to the intramolecular antiferromagnetic interaction between eight neighboring Co(II) ions making a circle with the interaction parameter on the order of  $J/k_{\rm B} \approx -10 \ {\rm cm}^{-1}$ .

Hydroboration of Ketones by SD/Co8a and SD/Co8b. The catalytic reduction of carbonyl compounds to alcohols is one of the most important chemical transformations in organic chemistry, which provides an invaluable tool in fine chemical production and natural product synthesis.<sup>20</sup> Although reduction of carbonyl compounds has been reported by precious metals,<sup>21</sup> main group elements,<sup>22</sup> rare earth metals,<sup>23</sup> and alkali metals,<sup>24</sup> catalytic carbonyl hydroboration remains relatively undeveloped by first-row earth-abundant transition-metal,<sup>22</sup> and which is currently of great interest. Some advances in modulating the selectivity or catalytic efficiency of catalysts have also been made for carbonyl hydroboration, but synergistic catalysis of hydroboration of unsaturated compounds using polynuclear transition metal clusters as catalysts has not yet been reported until now. Herein, the modeling trials were performed using SD/Co8a and SD/Co8b as homogeneous catalysts to explore the possibility of hydroboration of acetophenone with pinacolborane (HBpin).

Initially, we chose acetophenone as the model substrate to conduct the hydroboration reaction with HBpin in the presence of octanuclear Co(II)-silsesquioxane nanocages **SD**/**Co8a** and **SD**/**Co8b**. Acetophenone can be hydroborated to afford 2-(phenylethoxy)pinacolborane with 58% yield at a 2 mol % loading of **SD**/**Co8a** in *n*-hexane at 60 °C for 24 h (entry 1, Table 1). Encouraged by this initial result, we then focused our attention toward the optimization of the reaction conditions (Table 1). Various solvents were tested first (entries 1–4, Table 1), the reaction also proceeded very well in polar solvents such as CDCl<sub>3</sub> and THF, and the latter was found to be the best solvent, giving almost quantitative yield (entry 4, Table 1) as inferred from <sup>1</sup>H NMR analysis.

In order to check the influence of catalyst dosage on catalytic reaction efficiency, the reactions were further carried out with 1 mol % loading of **SD/Co8a**, which resulted in a slightly low yield (entry 5, Table 1). When shortening reaction time and lowering temperature (entries 6 and 7, Table 1), the yield of targeted products becomes quite low. Under the same

Table 1. Optimization of the Reaction Conditions<sup>a</sup>

		+ HBpin —	►	OBpin	
entry	cat. (mol %)	solvent	time (h)	temp (°C)	yield (%)
1 <sup>b</sup>	2	<i>n</i> -hexane	24	60	58
2 <sup>b</sup>	2	toluene	24	60	58
3 <sup>b</sup>	2	CDCI <sub>3</sub>	24	60	73
4 <sup>b</sup>	2	THF	24	60	99
5 <sup>6</sup>	1	THF	24	60	92
6 <sup>b</sup>	2	THF	12	60	45
7 <sup>b</sup>	2	THF	24	50	19
8 <sup>c</sup>	2	THF	24	60	99
9 <sup>c</sup>	1	THF	24	60	85
10 <sup>d</sup>		THF	24	60	4

<sup>a</sup>Reaction conditions: acetophenone (0.2 mmol), pinacolborane (HBpin) (0.22 mmol), **SD/Co8a** or **SD/Co8b** catalysts and 1,3,5-trimethoxybenzene (0.05 mmol, internal standard) in 0.5 mL of solvent. <sup>b</sup>**SD/Co8a** as catalyst. <sup>c</sup>**SD/Co8b** as catalyst. Yields were determined by <sup>1</sup>H NMR analysis based on acetophenone. <sup>d</sup>Without catalyst.

condition, however, **SD/Co8b** exhibited excellent catalytic performance (entry 8, Table 1). Thus, 2 mol % loading of **SD/Co8a** or **SD/Co8b** with a mild reaction temperature of 60 °C for 24 h in THF was determined as an optimized condition for the hydroboration of ketones. Control experiments also indicated that the hydroboration reaction can hardly proceed in the absence of catalyst under the same condition (entry 10, Table 1), which is consistent with the results reported in other studies.<sup>26</sup>

With the optimized reaction conditions in hand, a variety of commercially available ketones were subjected to the hydroboration reactions to study the substrate scope capabilities, and the results are presented in Table 2. Both aromatic and alkyl ketones can be hydroborated by SD/Co8a and SD/Co8b to boronate esters in moderate to excellent yields under the optimized conditions (64-99%). The electron-withdrawing and -donating groups, such as -CF<sub>3</sub>, -Cl, -Br, -NO<sub>2</sub>, and -OCH<sub>3</sub> groups, were tolerated on ketones substrates. In particular, the halogen group was keep intact in this protocol, which offered the possibility of further functionalization of the hydroborated products. Note that the ketones substrates with unsaturated functional groups such as nitro (entries 3 and 6, Table 2) selectively hydroborated C=O bond. When SD/ Co8a was used as catalyst for ortho-substituted substrates (entries 2 and 3, Table 2), the yields are diminished (64% and 85%) compared to para-substituted substrates (entries 5 and 6, Table 2), which clearly demonstrated the steric hindrance effect of substrates. Moreover, a series of compared catalytic experiments also indicated that the catalytic activities of SD/ Co8b are superior to those of SD/Co8a under same condition, as seen in entries 2, 3, and 8.

As mentioned before, octanuclear Co(II)-silsesquioxane nanocages **SD/Co8a** and **SD/Co8b** are paramagnetic in both solution and in the solid state, which precludes us to monitor the catalytic reaction process by NMR spectroscopy. To gain insights into the mechanism of this hydroboration reaction, ESI-MS was used to check the catalytic active species or intermediates by extracting the mother liquor after reaction proceeded for 1 h. We set three parallel experiments to examine the interactions between catalyst and reactants. When

Table 2. Hydroboratio	n of Ketones	Catalyzed	by SD	/Co8a
and SD/Co8b				

	$R^1 R^2 + HBpin$	<u><i>cat.</i> (2 mol%)</u> THF, 60°C, 24 h R <sup>1</sup>	DBpin <sup>∕</sup> R <sup>2</sup>
entry	substrate	product	yield (%)
1	CF3	OBpin CF <sub>3</sub>	>99% <sup>b</sup>
2	O CI	OBpin CI	64% <sup>b</sup> >99% <sup>c</sup>
3		OBpin NO <sub>2</sub>	85% <sup>b</sup> >99% <sup>c</sup>
4	O Br	OBpin Br	>99% <sup>b</sup> >99% <sup>c</sup>
5	CI	OBpin Cl	>99% <sup>b</sup> >99% <sup>c</sup>
6	O <sub>2</sub> N	OBpin O <sub>2</sub> N	>99% <sup>b</sup> >99% <sup>c</sup>
7		OBpin	71% <sup>b</sup> >99% <sup>c</sup>
8	O Br	OBpin Br	86% <sup>b</sup> 93% <sup>c</sup>
9	Br	Br	85% <sup>b</sup> 88% <sup>c</sup>
10	° L	OBpin	>99%c

<sup>47</sup>Reaction conditions: ketones (0.2 mmol), pinacolborane (HBpin) (0.22 mmol), catalysts **SD/Co8a** or **SD/Co8b** (2 mol %) in 0.5 mL of solvent. <sup>b</sup>**SD/Co8a** as catalyst. <sup>c</sup>**SD/Co8b** as catalyst. Yields were determined by <sup>1</sup>H NMR analysis based on ketones.

examining the ESI-MS of reaction solution of **SD/Co8b** and acetophenone in THF, we did not observed any peaks corresponding to the catalyst-ketone adducts (Figure S7a). However, the ESI-MS of reaction solution of **SD/Co8b** and HBpin clearly showed the peak of catalyst-borane adducts. By matching the experimental and simulated isotopic distributions, we can assign the dominant peak at m/z = 2479.0852 to  $[(SD/Co8b + HBpin) + Na)]^+$  (calcd m/z = 2479.0973, Figure S7b), which indicates the catalyst **SD/Co8b** can combine with one reactant to form active intermediates. We further examined the reaction solution of **SD/Co8b** + HBpin, and acetophenone by ESI-MS, but only **SD/Co8b** + HBpin adducts can be detected as well. The ESI-MS results

alternatively justified the stability and robustness of the cage cores during the catalytic reaction process. On the basis of the above observations, two possible hydroboration mechanisms tall



are proposed with different bond cleavage fashions around the

Figure 4. Proposed mechanisms for hydroboration by SD/Co8a and SD/Co8b.

Initially, catalyst-borane adducts formed by a Lewis acid cobalt center and an adjacent Lewis-basic N or O atoms in catalyst to ligate HBpin.<sup>27</sup> Subsequent catalyst-borane adducts were dissociated accompanying the transfer of borenium to the oxygen atom of substrate, which would then be susceptible to nucleophilic attack of the hydride released from cobalt hydride and regenerates the catalyst for further reaction. Considering the stronger Co–O bond strength, the hydroboration route (path a) involving the Co–N bond cleavage is the most possible.

In order to prove the stability of **SD/Co8a** during the catalysis reaction, we collected the solid sample of **SD/Co8a** after a 5-fold scaled-up catalytic reaction by rotating evaporation of solvent and measured PXRD patterns and IR spectrum (Figures S8 and S9), which matched well with those of pristine **SD/Co8a**, clearly indicating the robustness of catalyst in the reaction.

# CONCLUSIONS

In conclusion, two novel space craft-like octanuclear Co(II) nanocages based on two tetrameric silsesquioxane ligands assisted with pyrazole ligand have been fabricated and characterized. The ESI-MS was first introduced to the Co(II)-silsesquioxane system to illustrate their solution stability. The magnetic analysis show that **SD/Co8a** displays antiferromagnetic interactions between Co(II) ions. Moreover, both of them show excellent catalytic activity for hydroboration of ketones in the presence of pinacolborane under mild conditions. The catalytic reaction mechanism was also proposed by tracking the reactions using ESI-MS.

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b00137.

Figures, tables, IR and TGA data (PDF)

#### **Accession Codes**

CCDC 1882225–1882226 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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# Notes

The authors declare no competing financial interest.

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