Supplementary Information for:

Generating and Stabilization of Co(I) in a Nanocage Environment

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I. Experimental Procedures
General Procedures. Dry tetrahydrofuran, diethyl ether, toluene, and toluene-d8 were distilled from sodium/benzophenone ketyl. All other solvents (anhydrous), reagents and catalysts were purchased commercially and were used without further purification. Experiments involving core-shell nanosphere (II), nanocage (III), Co@III, and Co(ox)@III were performed using dry box or Schlenk techniques under a nitrogen atmosphere.

Analytical Methods. 1H and 13C NMR spectra were recorded with a Varian INOVA 400 spectrometer, operated at 400 MHz for 1H, 100 MHz for 13C. The 1H and 13C NMR chemical shifts are reported relative to SiMe4 and were determined by reference to the residual 1H solvent resonances. The chemical shifts reported are in ppm and coupling constants in Hz. FTIR spectra were taken on Thermo Nicolet NEXUS 670 FTIR. UV/vis spectra were taken using a Perkin Elmer LAMBDA 1050 in Keck Biophysics Facility supported from Northwestern University Office for Research, the NIH and the Rice Foundation. The cyclic voltammetry measurements were taken using a Data were collected with a CHI 600 Electrochemical Scanning Microscope (CH Instruments Inc.) in a one-compartment cell using a glassy carbon working electrode (diameter=3mm), a platinum wire counter electrode and a Ag/AgCl reference electrode. The electron paramagnetic resonance (EPR) spectra were collected at 9.36 GHz at 7K using a Bruker ESP300 with a helium Oxford flow cryostat under non-saturating conditions. The magnetism measurements were taken using a computer-controlled Quantum Design (http://www.qdusa.com) Magnetometer (MPMS5) in magnetic and physical properties measurement facility supported by the national science foundation.

II. NMR and IR spectra evidences for the hydrolysis of silyl ester bonds in II.
Isotope labeling experiment
The silyl ester bonds in II were cleaved by water. Both 24 equivalents of H2O and D2O were exposed to I, respectively. The samples were placed in J Young tubes under the protection of N2. The 1H NMR evidence as shown in Figure S1 supported the formation of –SiOH interior. The single peak at 2.5 ppm, which can be assigned as Si-OH, appeared in 1H NMR after the H2O treatment of II, indicating the formation of more silanol groups. Reactions between D2O and II did not show any new peak, suggesting that the formation of silanol groups was due to water treatment. All the other peaks were identical.

IR spectra of I, II and cleaved II
The FT-IR spectrum of the core shell nanosphere II shows an intense band at 1715 cm⁻¹ (δC=O in silyl ester bonds), while the core structure, I, has two δC=O bands at 1712 and 1721 cm⁻¹. After 24 h of hydrolysis with 24 equivalents of water (mol ratio H2O : nanocage = 24 :1) at 100 °C, the intensity of band at 1715 cm⁻¹ decreased and the other two bands appeared, indicating the formation of COOH groups. It should be noted that other peaks in the FT-IR spectra characteristic of the carbosilane shell, such as the CH3 deformation in Si-CH3 at 1250 cm⁻¹, and the peak for p-substituted silphenylene at 1135 cm⁻¹, Si-CH3 rocking, and CH deformation at 750-870 cm⁻¹ did not change after hydrolysis, suggesting that the shell was stable (Figure S2).
Figure S1 NMR spectra of: II (black line), II after H$_2$O treatment, (blue line), II after D$_2$O treatment, (red line). Except for the formation of carboxylic acid and silanol as indicated, all other peaks are identical.
Figure S2 FT-IR spectra of: a) core – shell nanosphere II, b) hydrolytically cleaved II, and c) I. Changes in the carboxylic acid/carboxylate peak at 1700-1800 cm$^{-1}$ are magnified for clarification.
III. The IR spectra of the reactions between III and Co$_2$(CO)$_8$

Figure S3. IR spectra of: a) III, b) after reaction of III with 1 equivalent of Co$_2$(CO)$_8$, c) with 4 equivalents of Co$_2$(CO)$_8$, and d) with 12 equivalents of Co$_2$(CO)$_8$.

Figure S4. IR spectra of: a) II, b) after mixing II and Co$_2$(CO)$_8$, c) after reaction of III with Co$_2$(CO)$_8$. 
IV. The NMR spectra of III and IV.

**Figure S5.** $^1$H NMR spectrum of: a) Co@III, and b) III in dry toluene-$d_8$.

V. Cyclic voltammetry measurement of IV

**Figure S6.** Cyclic voltammograms of a THF solution of 2.5mM of Co$_2$(CO)$_8$ and 1 mM ferrocene (as internal standard) (red line), and of 1.7 mM of Co@III (i.e.~5.1 mM of Co, assuming 3 Co per III) and ferrocene (blue line). The sweep rate $\nu$ =0.05 Vs$^{-1}$.
VI. Determination of the stoichiometry of cobalt and coordinated CO by thermal decomposition of Co@III

To determine the absorption coefficient $\varepsilon$ of CO in the gas phase, CO/He gas mixtures with different volume% of CO were passed through a gas cell (L = 21.5cm) at room temperature. The IR spectra were collected using a Nicolet Nexus 670 FTIR spectrometer and 1 cm$^{-1}$ resolution. As shown in Figure S5, the small peak at 2227.4 cm$^{-1}$ was chosen for measurement to avoid the saturation of the detector and nonlinearity. The data, displayed in Table S1 and plotted in Figure S6, showed that the absorbance was linearly dependent on the concentration. Using this plot and Beer-Lambert Law, the proportionality constant between absorbance, CO concentration, and path length was calculated.

![Figure S7. A typical IR spectrum of CO gas](image)

Table S1. Values for calculating the absorption coefficient ($\varepsilon$)

| Intensity | Relative Concentration of CO ($V_{CO}/V_{total}$) |
|-----------|-----------------------------------------------|
| 0.027     | 0.01316                                       |
| 0.030     | 0.01572                                       |
| 0.038     | 0.02078                                       |
| 0.048     | 0.02797                                       |
| 0.075     | 0.05                                          |
Figure S8. The plot of absorbance as a function of CO concentration in the gas phase.

In the actual experiment to determine the CO/Co stoichiometry in Co@III, 6.962*10^{-3} mmol of Co@III (0.028mmol Co) was loaded into the gas cell of L = 11cm in a dry box. The IR cell with the sample was evacuated and backfilled with nitrogen three times. It was then filled with about 1 atm of He and heated up to about 80°C in the IR instrument. Typical IR spectra during the thermal decomposition process are shown in Figure S9. The spectra were monitored as a function of time until no further changes could be detected. In the final spectrum, the peak at 1958 cm^{-1} disappeared and the absorbance of the peak at 2227.4 cm^{-1} was 0.007. The total volume of this chamber is 53.97ml with a length of 11 cm. From the proportionality constant determined in Figure S8, the optical path length of 11 cm, and assuming ideal gas law (PV = nRT, where the pressure = 1 atm), the amount of CO formed was calculated to be 0.024 mmol, closed to the theoretical value of 0.028 mmol for a Co : CO of 1:1.
Figure S9. IR spectra of the gas phase above a Co@III solid during thermal decomposition at 80°C. (a) Three spectra of increasing time of decomposition, starting with the beginning for the bottom curve, and increasing time for the next two spectra. (b) The difference spectra between the last and first spectrum.

VII. EPR and Magnetism measurements of Co@III and Co(ox)@III

EPR spectra were collected at 9.36 GHz at 7K using a Bruker ESP300 with a helium Oxford flow cryostat under non-saturating conditions. Quantification of paramagnetic cobalt was performed by comparison to a Co(II) standard prepared at 1 mM. The spectra of Co@III and Co(ox)@III are shown in Figure 2A and B, respectively. The spectrum is typical of a high-spin (S=3/2) Co(II). The small signal at g ~2 is from a small Cu(II) impurity. The concentration of Co(II) is determined by double integration of the EPR spectrum and compared to a Co(II) standard, prepared at 1 mM. The sample before exposure to O₂ contains a small amount of Co(II) (0.1 mM) and increases to 0.7 mM after 90 minutes of O₂ exposure.

The magnetism measurements were taken using a computer-controlled Quantum Design Magnetometer (MPMS5) in magnetic and physical properties measurement facility supported by the national science foundation. The temperature dependent mass magnetic susceptibilities (χₘ) of Co@III and Co(ox)@III were fitted using Curie – Weiss law (χₘ = C/(T - Θ)), where C is the Curie constant, T is the absolute temperature and Θ is the Weiss constant). Room-temperature molar magnetic susceptibilities (χₘ) in the solid state were calculated with the assumption that all the cobalt centers have no interaction with each other and homogeneously dispersed in the nanocage. The molecular weight of one Co in Co@III was calculated as 8248/4 = 2062 g/mol, while that in Co(ox)@III was 8204/4 = 2051. They were corrected for diamagnetism using Pascal constants and converted into effective magnetic moments.1
VIII. Reaction of Co@III with O₂

Figure S10. UV-vis spectra of: (a) Co₂(CO)₈ and Co@III in toluene (concentration 3.7 * 10⁻⁵ M); (b) after exposure of Co@III to O₂; (c) complexes Co@III (black line) and Co(ox)@III (blue line).
Table S2. Data for rate constant determination.

| Time (min) | Abs of the band at 396nm | Concentration of Co@III (M) | ln[Co@III] |
|------------|--------------------------|----------------------------|------------|
| 0          | 2.23                     | 3.7*10^{-5}                | -10.2046   |
| 40         | 1.17                     | 1.94126*10^{-5}            | -10.8496   |
| 50         | 1.04                     | 1.72556*10^{-5}            | -10.9674   |
| 60         | 0.96                     | 1.59283*10^{-5}            | -11.0474   |
| 70         | 0.83                     | 1.37713*10^{-5}            | -11.1929   |
| 80         | 0.74                     | 1.2278*10^{-5}             | -11.3077   |

The data in Table S2 were collected using a cuvette about half-filled with a toluene solution of Co@III (~3 mL). The overhead space (~3 mL) was filled with dioxygen (10% O2 in He). Exposure to this excess amount of dioxygen caused disappearance of the orange color. The initial concentration of the solution was ~3.7 * 10^{-5} mmol/ml. Changes in the band at 396 nm (ε = 6.27* 10^{-5} M^{-1}·cm^{-1}) were followed as a function of time using UV-vis (Figure S10 (b)). The reaction follows the pseudo- first order with the rate constant of 0.014 min^{-1}. The half-life of Co@III can be calculated as 49.4 min. In the end of the reaction, the color of the solution changed to blue-purple.

In-situ FT-IR spectroscopy on the reaction between O2 and Co@III was taken using a customized IR chamber. No significant change except the disappearance of the CO peak was observed.
Figure S12. IR spectra of Co@III as a function of time before and after exposure to O₂. Except for the gradual disappearance of the 1958 cm⁻¹ band, the rest of the spectrum remained unchanged.

The solution after the reaction between O₂ and Co@III was analyzed for H₂O₂. In air, 3 mL H₂O was added to the reaction mixture (4*10⁻⁴ mmol Co in 3 mL toluene + 3 mL H₂O). After about 30 min, the water phase was separated from the toluene phase. Titration of H₂O₂ was performed using potassium titanium oxalate.³ In this method, the aqueous layer was mixed with 1 mL stock sulfuric acid solution and 1 mL potassium titanium oxalate stock solution. The H₂O₂ reacted with potassium titanium oxalate to form an intensely yellow complex of pertitanic acid and H₂O₂, which possessed a characteristic UV-vis band at 390 nm. From the intensity of this band and the calibration curve (Table S3 and Figure S13), the concentration of H₂O₂ was detected to be ~0.004 mg, or ~0.82 mg/L, which was 59% yield.

Table S3. Data for the amount of H₂O₂ determination (L = 1 cm).

| Calibration sample | Abs of the band at 390 nm | Concentration of H₂O₂ (mg/L) |
|--------------------|--------------------------|------------------------------|
| 1                  | 0                        | 0                            |
| 2                  | 0.02                     | 0.8                          |
| 3                  | 0.033                    | 1.6                          |
| 4                  | 0.054                    | 2.4                          |
| 5                  | 0.073                    | 3.2                          |
| 6                  | 0.09                     | 4.0                          |
Figure S13. Plot of absorbance by standard solutions for the determination of H_2O_2 concentration (L = 1cm).

VIII. Reaction between Co_2CO_8 and POSS-(OSiMe_2CH_2CH_2CH_2CH(COOH)_2)_8 (I)

The core compound, POSS-(OSiMe_2CH_2CH_2CH_2CH(COOH)_2)_8, was treated with 4 or 8 equivalents of Co_2(CO)_8 in a mixture of toluene and THF (20 : 1 volume ratio). The reactions were allowed to stir for two days at room temperature. Concentration of the solution afforded pink precipitate as the major products in about 90% yield based on the amount of POSS-(OSiMe_2CH_2CH_2CH_2CH(COOH)_2)_8. The amount of cobalt precursor did not affect the yield.

Figure S14. SEM picture of the pink product from the reaction between I and Co_2CO_8.
Figure S15. FT-IR spectra of (a) the pink product from the reaction between I and Co$_2$CO$_8$ and (b) POSS-(OSiMe$_2$CH$_2$CH$_2$CH$_2$CH(COOH)$_2$)$_8$

Figure S16. XPS spectra of the pink product from the reaction between Co$_2$CO$_8$ and I. The XPS spectrum of the pink product is similar to those of Cobalt (II) acetate complexes related samples$^2$. 

X. Reaction between Co@III and organoazides

Figure S17. UV-vis spectra of Co@III before (black) and after reaction with phenyl azide (blue).

Reference

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