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Calixarene-Mediated Synthesis of Cobalt Nanoparticles: An Accretion Model for Separate Control over Nucleation and Growth

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Abstract

The nucleation and growth of crystalline cobalt nanoparticles (Co NPs) under solvothermal conditions can be separated into distinct stages by using (i) polynuclear clusters with multivalent capping ligands to initiate nucleation, and (ii) thermolabile organometallic complexes with low autonucleation potential to promote crystalline growth. Both nucleation and growth take place within an amorphous accretion, formed in the presence of polyvalent surfactants. At the pre-nucleation stage, a calixarene complex with multiple Co₂-alkyne ligands (Co₁₆-calixarene **1**) undergoes thermal decomposition above 130 °C to form “capped cluster” intermediates that coalesce into well-defined Co nanoclusters, but are resistant to further aggregation. At the post-nucleation stage, a monomer (pentayne-Co₄(CO)₁₀, or PTC) with a low thermal activation threshold but a high barrier to autonucleation is introduced, yielding ε-Co NPs with a linear relationship between particle volume and the Co mole ratio ([Co_{final}]/[Co_{seed}]). Co nanocrystals can be produced up to 40 nm with a 10–12% size dispersity within the accretion, but their growth rate depends on the activity of the supporting surfactant, with an octapropargyl calixarene derivative (OP-C11R) providing the most efficient transport of reactive Co species through the amorphous matrix. Post-growth digestion with oleic acid releases the Co NPs from the residual accretion, which can then self-assemble by magnetic dipolar interactions into flux-closure rings when stabilized by calixarene-based surfactants. These studies demonstrate that organometallic complexes can be designed to establish rational control over the nucleation and growth of crystalline NPs within an intermediate accretion phase.

Introduction

Nanoparticles with strong magnetic moments are essential for many applications in nanomaterials science and engineering.^{1, 2, 3} Magnetic nanoparticles (MNPs) are desirable as materials in nonvolatile data storage and spintronics,^{4,5} in analyte concentration and separation,^{6,7} as actuators in drug delivery systems,^{8, 9} and as contrast agents in biological imaging modalities.^{10,11,12} All of these endeavors can be further advanced by robust methods for preparing crystalline MNPs with precise control over size and shape, which

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Supporting Information. ATR-IR and TGA analysis of **1** and PTC; additional TEM images of Co NPs; chemical characterization data for **1**, OP-C11R, and PTC. This material is available free of charge via the Internet at <http://pubs.acs.org>.

have fundamental relationships with total magnetic moment, magnetocrystalline anisotropy, and blocking temperature.¹ The magnetic anisotropy energy for MNPs is expressed as $E = K_u V \sin^2 \theta$, where K_u represents the uniaxial magnetic anisotropy constant and θ is the angle between the easy axis and the direction of the applied field. Size is also important in the thermoremanent behavior of composite materials comprised of single-domain MNPs, as the Néel relaxation for thermoremanent magnetization increases exponentially with grain volume V .^{13,14}

While many excellent methods for synthesizing MNPs exist, most are designed for sizes below 20 nm and use surfactants to limit growth rates. Thermoremanent MNPs are typically greater than 20 nm in diameter, but the controlled synthesis of larger NPs is less predictable and generally optimized using empirical means. For example, digestive ripening offers a thermodynamic approach for producing colloids of narrow size dispersity,^{15,16,17} although the end results between batches are often variable. Stepwise seeded growth is an attractive alternative, as the reactivity and composition of the nuclei and growth agents can be adjusted independently, but NP nuclei are often prepared separately prior to postnuclear growth. A third possibility is to design molecular agents whose reactivities are tailored specifically for nucleation *or* growth. In principle, the pairing of such species during NP synthesis offers modular control over size and concentration in a single step, if secondary growth processes can be controlled.

In this paper, we show that organometallic precursors can promote NP nucleation or growth under solvothermal conditions on the basis of their thermochemical profiles, with application toward the size-controlled synthesis of Co NPs in the range of 6–40 nm. Cobalt has high magnetic anisotropy ($K_u(\text{fcc-Co}) = 4.5 \times 10^6 \text{ erg/cm}^3$) and can exhibit single-domain behavior for sizes up to 70 nm.^{18,19} Co NPs also have catalytic activity^{20,21} and can be used as templates for the synthesis of hollow gold or chalcogenide nanoshells, based on the Kirkendall effect.^{22,23} Numerous conditions for the synthesis of Co NPs have been reported,^{24,25,26,27,28} but in most cases the nucleation and growth phases were not fully separated, particularly when using thermolabile reagents such as $\text{Co}_2(\text{CO})_8$.^{17,24,27}

Our reactants for controlled nucleation and growth are based on Co_{16} -calixarene **1**, a multivalent calixarene platform with Co_2 -alkyne ligands, and pentyne- $\text{Co}_4(\text{CO})_{10}$ (PTC), a cobalt-rich species with low autonucleation potential (Figure 1). We previously demonstrated that polynuclear Co-calixarene complexes could produce 3–4 nm Co NPs that were stable to further aggregation or digestive ripening.²⁹ In this study, we show that calixarene-stabilized nanoclusters can nucleate NP formation in PTC mixtures, to produce Co NPs of controlled size up to 40 nm. We also demonstrate a stoichiometric relationship between NP volume and added growth agent, as evidence for separate control over nucleation and growth.

We further observe that in the presence of mild surfactants, Co_{16} -calixarene **1** and PTC initially condense into an amorphous matrix or accretion, followed by the gradual growth of crystalline Co NPs with low size dispersity. The accretion phase is consumed during Co NP growth, but can be sustained by the continuous addition of PTC to the reaction mixture. The migration of reactive Co species to the NP cores embedded within the intermediate accretion

is assisted by mild, polyvalent surfactants such as C11 resorcinarene (C11R) and especially octa-*O*-propargyl C11 resorcinarene (OP-C11R), whereas digestive surfactants such as oleic acid can dispel the accretion to enable the release and dispersion of the Co NPs.

Experimental Section

Reagents

Co₂(CO)₈ and Co₄(CO)₁₂ were purchased from Strem and stored neat under anaerobic conditions. Solutions of Co₂(CO)₈ and Co₄(CO)₁₂ were freshly prepared in anhydrous *o*-dichlorobenzene (ODCB) and passed through a 0.2-μm PTFE filter to remove particulates, then deaerated with argon gas prior to use. Tetra-*C*-undecyl calix[4]resorcinarene (C11R) was synthesized in multigram quantities by a previously described procedure,³⁰ but using methanol as the solvent and 5:1 hexanes:acetone for recrystallization. All other reagents were obtained from commercial sources and used without further purification unless otherwise specified.

Analysis

Transmission electron microscope (TEM) images were acquired using a Philips CM-10 operating at 80 kV, a Philips CM-100 operating at 100 kV, a FEI Tecnai F20 operating at 200 kV, and a FEI Titan ETEM operating at 300 kV. The latter was used to obtain energy-filtered TEM images of carbon, cobalt, and oxygen using electron energy loss spectroscopy (EELS). TEM samples were prepared by the tenfold dilution of as-synthesized particles, followed by 1 min sonication prior to their deposition on carbon-coated 400-mesh Cu grids. Particle size analysis was performed using commercial software (SigmaScan Pro5) on TEM images obtained directly from a digital camera or on scanned images captured on negative films (800 dpi). Statistical analyses were based on a minimum of 100 particles per sample, unless otherwise stated. In most cases the particles were assumed to be spherical, with diameter and volumes based on a single width measurement ($V = \pi d^3/6$). In the case of samples with a significant population of cube-shaped particles, the same method was applied but supplemented by a volumetric analysis of cubic particles using edge length ($V = d^3$).

Matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) was performed using an Applied Biosystems Voyager DE Pro. Samples and reaction mixtures were spotted on stainless steel plates precoated with *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (synonym: DCTB) and dried under vacuum, just prior to analysis. Infrared (IR) analyses were performed on thin films deposited on a ZnSe window, using a Nexus 670 spectrometer (Thermo) equipped with a grazing-angle attenuated total reflectance module (GATR, Harrick) and coupled to a purge gas generator to remove atmospheric CO₂ and moisture. Thermogravimetric analyses (TGA) were performed with a Q500 TA instrument at a heating rate of 2 °C/min under nitrogen. ¹H and ¹³C NMR spectra were obtained using a Varian 300 MHz or a Bruker 400 MHz spectrometer, with chemical shifts reported in parts per million (ppm). All temperatures were measured with a resolution of 1–2 °C.

Pentyne–Co₄(CO)₁₀ (PTC)

1-pentyne (0.4 mL, 4.06 mmol) and Co₄(CO)₁₂ (500 mg, 0.87 mmol) were dissolved in 8 mL of deaerated CHCl₃, then heated to 55 °C and stirred for 5 hours under argon, then concentrated and purified by silica gel chromatography using a 10:1 mixture of hexanes and CH₂Cl₂ to yield the desired complex as a dark blue solid (430 mg, 85% yield). ¹H NMR (300 MHz, C₆D₆): δ 7.48 (s, 1 H), 2.33 (t, 2 H, *J* = 8 Hz), 1.03 (sextet, 2 H, *J* ~7.5 Hz), 0.64 (t, 3 H, *J* = 7 Hz). ¹³C NMR (100 MHz, C₆D₆):³¹ δ 138 (broad), 109.0, 55.85, 29.9, 14.0. ATR-IR (cm⁻¹): 2963, (w), 2929 (w), 2871 (w), 2092 (s), 2046 (vs), 2019 (vs), 1999 (vs), 1967 (s), 1862 (vs), 1461 (w), 1454 (w), 1432 (w), 1375 (w), 1338 (w), 1287 (w), 1266 (w). Key bond lengths and angles from x-ray crystallographic analysis are reported in Supporting Information.

Octa-O-propargyl C11 resorcinarene (OP-C11R)

C11R (2.01 g, 1.81 mmol) was dried by azeotropic distillation with toluene, then dissolved in 18 mL of anhydrous DMF under argon and treated with powdered K₂CO₃ (4.98 g, 36.2 mmol) and Bu₄NI (134 mg, 0.36 mmol). The reaction mixture was stirred for 5 min, then treated with propargyl chloride (1.3 mL, 18.1 mmol). The reaction was heated to 60 °C and stirred for 12 hours, then quenched at 0 °C with NH₄Cl solution and extracted with Et₂O. The organic phase was washed with H₂O and brine, dried over Na₂SO₄, concentrated under reduced pressure, and purified by silica gel chromatography using a 0–15% EtOAc–hexanes gradient with 0.1% Et₃N to afford OP-C11R as a white solid (1.78 g, 69% yield). ¹H NMR (400 MHz, CDCl₃): δ 6.69 (s, 4 H), 6.63 (s, 4 H), 4.49 (t, 4 H, *J* = 7.4 Hz), 4.38 (dd, 16 H, *J* = 2.3, 5.3 Hz), 2.47 (t, 8 H, *J* = 2.3 Hz), 1.81 (d, 8 H, *J* = 6.4 Hz), 1.37–1.19 (m, 72 H), 0.91–0.84 (m, 12 H). ¹³C NMR (100 MHz, CDCl₃): δ 154.3, 128.6, 126.4, 101.7, 80.0, 77.5, 77.2, 76.8, 74.9, 57.6, 35.4, 34.9, 32.1, 30.1, 30.0, 29.9, 29.6, 28.1, 22.9, 14.3. ATR-IR (cm⁻¹): 3307, 2921, 2581, 2125, 1608, 1504, 1295, 1037. ESI-MS: *m/z* calcd for C₉₆H₁₂₈O₈Na [M+Na]⁺ 1432.0, found 1432.6.

Octakis[propargyl–Co₂(CO)₆]C11 resorcinarene (1)

Co₂(CO)₈ (205.2 mg, 0.60 mmol) and OP-C11R (84.4 mg, 0.060 mmol) were dissolved in deaerated hexanes (20 mL), stirred for 22 hours, then concentrated and purified by silica gel chromatography using 10% CH₂Cl₂ in hexanes to afford Co₁₆–calixarene **1** in 93% yield. ¹H NMR (300 MHz, CDCl₃): δ 6.63, 6.30–6.17, 5.87 (br), 5.31 (m), 4.76 (br), 4.62 (t, *J* = 7 Hz), 1.82 (br), 1.72 (br), 0.87 (t, *J* = 6.5 Hz).³² ¹³C NMR (100 MHz, CDCl₃): δ 199.2, 154 (br), 128.0, 127.7, 127.5, 89.3, 73.0, 70.4, 35.7, 35.4, 31.9, 30.2, 29.7, 29.3, 28.1, 22.6, 14.0. ATR-IR (cm⁻¹): 2963 (w), 2929 (w), 2871 (w), 2092 (m), 2046 (s), 2019 (vs), 1999 (vs), 1967 (s), 1862 (vs), 1461 (w), 1454 (w), 1432 (w), 1375 (w), 1338 (w), 1287 (w), 1266 (w).

Seeded growth experiments using pristine Co nanocrystals

In a typical experiment, Co₄(CO)₁₂ (50 mg, 0.087 mmol) in deaerated ODCB (5 mL) was injected into a refluxing solution of ODCB (2 mL) containing oleic acid (40 μL, 0.13 mmol). The reaction mixture was kept at reflux for 15 min, then cooled to room temperature to produce oleic acid-stabilized Co nanocrystals with size dispersities of 10–12% (mean

diameter = 4.7 ± 0.6 nm). The seed solution was extracted with an airtight syringe until 1 mL remained (ca. 10^{15} particles), which was then heated to 130 °C and treated with a deaerated solution of PTC and C11R in ODCB. All seeded growth experiments were characterized by TEM analysis.

Co nanoparticle formation using **1** and PTC as nucleation and growth agents

All experiments were performed at a constant stirring rate to avoid possible perturbations due to differences in shear force. In a typical experiment, Co₁₆-calixarene **1** (8 mg, 0.035 mmol Co) was dissolved in 2 mL of deaerated ODCB containing C11R (0.74 mg, 0.66 μ mol) or OP-C11R (0.95 mg, 0.66 μ mol) as a stabilizing surfactant. The mixture was heated at 130 °C for 20 min, ramped to 180 °C over 20 min, then stirred at 180 °C for 1 h. PTC (115.3 mg, 0.80 mmol Co) was dissolved in 4 mL of ODCB containing C11R (16.8 mg, 19.33 μ mol) or OP-C11R (21.4 mg, 19.33 μ mol), and added to the reaction mixture by syringe pump over 1 h. The reaction mixture was cooled and diluted 10 $\times$ with EtOH, with overnight exposure to a strong magnet to precipitate the Co NPs. These were redispersed in 5 mL toluene containing 10 mM oleic acid to achieve a particle density of ca. 10^{12} NPs/mL (estimated from initial weight of reagents), then heated for 2 h at reflux under argon to remove residual amorphous Co.

Results and Discussion

1. Polynuclear calixarene complexes as nucleating agents

Earlier studies have established that multivalent calixarenes can provide a useful platform for controlling nucleation events during NP synthesis.^{33,34,35,36} We have also obtained evidence that prenuclear “capped cluster” intermediates are generated by the thermolysis of *octakis*-[propargyl]-Co₂(CO)₆]tetra-*C*-methyl resorcinarene (Co₁₆-C1R), a truncated version of **1**.²⁹ Briefly, heating Co₁₆-C1R in refluxing ODCB and in the presence of oleic acid produced Co NPs below 4 nm, presumably via coalescence of capped-cluster intermediates. The calixarene-stabilized Co NPs were resistant to digestive ripening or aggregative growth after prolonged heating; in contrast, Co nanoclusters coated with monovalent alkynes increased in mean size and polydispersity when kept under similar conditions.

A similar experiment was performed with Co₁₆-C11R (**1**), except that oleic acid was replaced with C11R, which we have previously used as a nonionic surfactant for Co NPs.^{37,38} Calixarenes have proven to be excellent stabilizing agents of colloidal species in organic solvents,³⁹ and are thus well suited to support NPs at different phases of their synthesis. Complex **1** was dissolved in ODCB containing 0.33 mM C11R, and heated to temperatures from 130 °C ($t = 20$ min) to 180 °C ($t = 1$ h). TEM analysis of the reaction products at different temperatures indicated NP formation with a mean size of 2.9 nm at 130 °C and 3.6 nm at 180 °C (Figure 2), both smaller than those produced in the presence of oleic acid.²⁹ This confirmed that multivalent ligands such as calixarenes are excellent platforms for promoting nucleation, and for protecting nanoclusters from postnuclear aggregation.

TEM analysis also indicated that the Co NPs were not freely dispersed, but remained embedded in a persistent but amorphous accretion. This matrix is likely derived from the

crosslinking of the calixarene ligand in **1** (namely OP-C11R), either as a multivalent Co_n -alkyne coordination network or as a covalent network via Co-mediated Pauson–Khand mechanisms.⁴⁰ The accretion is sensitive to shear forces generated during magnetic stirring, but appears to be stable in the presence of C11R. ATR-IR analysis of **1** after thermolysis under anaerobic conditions at 130 °C for 20 min and 180 °C for 1 h revealed incomplete decarbonylation (40% and 6.7% respectively, by CO peak area integration) as well as a new stretching mode at 1874 cm^{-1} , suggestive of bridging μ -CO ligands on higher-order Co clusters (Figure S1, Supporting Information).^{41,42} Decarbonylation was also incomplete in the presence of C11R but was more efficient with oleic acid, which reduced the relative CO signal intensities to <1% after heating at 180 °C. These studies indicate that C11R has milder surface activity than oleic acid, which is well known to promote the digestion of organocobalt species as well as Co NPs.^{43,44} Surfactant effects on NP growth within the accretion will be discussed in a later section.

To determine whether Co_{16} -calixarene **1** was predisposed toward forming discrete “capped cluster” intermediates, we used MALDI-MS analysis to characterize ligand-stabilized nanoclusters of well-defined mass.^{45,46} MALDI-MS analysis of **1** in DCTB revealed a strong m/z peak corresponding with a decarbonylated complex ($\text{OP-C11R} + 16 \text{ Co}$; m_w 2352), and peaks corresponding roughly with dimer, trimer, and tetramer (Figure 3a). Samples of **1** heated between 50 °C and 130 °C in ODCB over a 75-minute period were also analyzed by MALDI-MS, which produced similar mass distribution profiles (Figure S2, Supporting Information) but did not reveal m/z peaks corresponding with larger Co-calixarene oligomers ($N > 5$). This suggests that the formation of calixarene-capped Co clusters is facile, but the kinetic product distribution does not depend strongly on reaction temperature, at least during the first hour.

It is interesting to note that m/z differences between mode peaks (as determined from Gaussian curve fits) range from 1850 to 2100, less than that expected from the simple clustering of decarbonylated **1**. The simplest explanation is the ejection of multiple Co atoms from Co_n -calixarene oligomers; for example, a m/z increase of 1880 corresponds with the addition of $\text{OP-C11R} + 8 \text{ Co}$. This argument is supported by a close inspection of m/z peaks within the molecular ion signal: several sets of peaks are separated by differences of 58–59, corresponding with the loss of neutral Co atoms (Figure 3b). Mass differences of 39 are also observed, suggesting the additional loss of a propargyl group ($\text{HC}\equiv\text{CCH}_2$) complexed with Co. The MALDI-MS observations imply that prenuclear Co-calixarene clusters may favor lower metal–ligand ratios for thermodynamic stability.

2. Selection of growth agent with low autonucleation potential

To complement the prenucleation conditions developed above, we sought a reagent with sufficient reactivity to promote efficient NP growth under solvothermal conditions, but with a relatively high barrier to autonucleation. We thus designed a seeded growth experiment that introduces the growth reagent to dispersions of preformed nanoclusters of known size, with two criteria in mind: (i) a uniform increase in NP size with little or no increase in polydispersity, and (ii) a linear relationship between the increase in mean particle volumes ($V_{\text{final}}/V_{\text{seed}}$) and the molar ratio of cobalt ($[\text{Co}_{\text{final}}]/[\text{Co}_{\text{seed}}]$), before and after growth. We

consider stoichiometric control in particle size to be a useful parameter for seeded growth, as it depends strongly on the efficiency of converting the growth reagent into metal NPs.

Initial growth studies were performed using freshly prepared Co nanocrystals in ODCB generated by the thermolysis of $\text{Co}_4(\text{CO})_{12}$ in the presence of oleic acid, which reliably produced nanoparticles with size dispersities of 10–12% (see Experimental Section). The pristine nanocrystals were subsequently treated at 130 °C with different mole ratios of organocobalt reagents, namely $\text{Co}_2(\text{CO})_8$, η_2 -pentyne- $\text{Co}_2(\text{CO})_6$, $\text{Co}_4(\text{CO})_{12}$, and η_2 -pentyne- $\text{Co}_4(\text{CO})_{10}$ (PTC). Thermogravimetric analysis (TGA) of these Co_2 and Co_4 species suggested a broad range of activation barriers for growth, with threshold decomposition temperatures (T_d at 10% wt loss) of 50, 160, 100, and 135 °C respectively (Figure S3, Supporting Information). It should be noted that TGA and T_d are rather simple indicators of thermal activation, as the weight loss depends on the heating profile. For example, heating PTC at a constant rate (2 °C/min) between 25 and 300 °C resulted in a 60% wt loss, indicating complete decomposition to bulk Co, whereas TGA performed on PTC previously heated for 20 min at 130 °C produced only a 15% weight loss, because most of the decomposition had taken place prior to analysis.

The reagent with the highest thermolability, $\text{Co}_2(\text{CO})_8$, provided poor size control during seeded growth at 130 °C or higher, with TEM analysis indicating a broad size distribution including particles below 5 nm. This result is not surprising, as $\text{Co}_2(\text{CO})_8$ has a well-known propensity for autonucleation under thermal conditions.^{24,47} The least thermolabile reagent, η_2 -pentyne- $\text{Co}_2(\text{CO})_6$, proved to be rather inert with respect to either autonucleation or seeded growth. We note that in the case of multivalent Co_{16} -calixarene **1**, its facile decomposition into the putative capped-cluster intermediate is promoted by the proximity of adjacent η_2 -alkyne- Co_2 units, prior to its coalescence into the observed Co nanoclusters (Figure 1).^{28d,29} On the other hand, alkyne- Co_2 complexes are much less reactive when used as postnuclear growth reagents.²⁶

We next examined the tetranuclear Co species $\text{Co}_4(\text{CO})_{12}$, which is more stable than $\text{Co}_2(\text{CO})_8$ and is considered as an intermediate *en route* to Co NP formation.^{24a,26,43} Co_4 species are not often used in Co NP synthesis,^{29,47,48} yet TGA shows the activation temperature of $\text{Co}_4(\text{CO})_{12}$ to be remarkably low ($T_d = 100$ °C). We thus performed sequential injections of saturated $\text{Co}_4(\text{CO})_{12}$ in ODCB into a heated solution containing 3.6-nm seeds and oleic acid, with stepwise increases in size to 5.3 and 6.5 nm (Figure S4, Supporting Information). Unfortunately, the low solubility of $\text{Co}_4(\text{CO})_{12}$ (10 mg/mL in ODCB) prevented further consideration as a practical growth agent.

We then considered η_2 -alkyne- $\text{Co}_4(\text{CO})_{10}$ derivatives as highly soluble Co_4 species. In particular, we favored pentyne- $\text{Co}_4(\text{CO})_{10}$ (PTC) for its high cobalt-to-mass ratio (40 wt% Co), similar to that of $\text{Co}_4(\text{CO})_{12}$. PTC was easily prepared from 1-pentyne and $\text{Co}_4(\text{CO})_{12}$ in 85% yield and recrystallized from hexanes as dark blue crystals, and observed to be stable at room temperature. X-ray crystallography of this alkyne- Co_4 complex revealed a distorted octahedron with the four Co atoms adopting the so-called butterfly structure (Figure 4), similar to those measured in earlier studies of alkyne- Co_4 species.^{49,50,51} The C-Co σ -bond lengths of PTC are similar to those of tetrahedral η_2 -alkyne- Co_2 complexes (mean value

1.97 Å),^{41,52} but the C–Co π -bond lengths are 3–8% longer, which may contribute toward the greater thermolability of the alkyne–Co₄ complex (Table S1, Supporting Information). TGA of PTC indicated a T_d of 135 °C, which correlated with sluggish and erratic growth behavior when heated at that temperature in ODCB (see below). We thus evaluated PTC as a candidate for the seeded growth of Co NPs.

To determine whether stoichiometric control over NP size could be achieved using PTC as a growth agent, a 0.2 M solution in ODCB was injected multiple times at 40-minute intervals into a reaction flask containing pristine Co nanocrystal seeds and C11R at 130 °C, with small aliquots removed in between additions for TEM analysis (Figure S5, Supporting Information). The Co mole ratio after each injection of PTC relative to the amount of Co₄(CO)₁₂ used for nucleation, $[\text{Co}_{\text{final}}]/[\text{Co}_{\text{seed}}]$, ranged from 3.4 to 27.4. Gratifyingly, we observe a nearly linear correlation between the increase in Co mole ratio and Co NP volume (Table 1); the relative errors for the final NP volumes are ~30%, based on the polydispersities in NP diameters. It is worth noting that the Co NPs were exposed to air during sample preparation for TEM analysis, possibly resulting in surface oxidation and size changes due to lattice expansion. This can introduce a larger measurement error when estimating size and volume (especially for smaller NPs), and can also result in smaller than expected volume ratios when compared with larger NPs. Despite this, the changes in $V_{\text{final}}/V_{\text{seed}}$ versus $[\text{Co}_{\text{final}}]/[\text{Co}_{\text{seed}}]$ correlate remarkably well.

To determine whether PTC was capable of self-nucleation, a solution of PTC and C11R was passed through a membrane filter and heated to 130 °C for 60 min in ODCB. This mixture first decomposed into an amorphous accretion, followed by the formation of Co NPs with a broad size distribution, surrounded by a residual accretion matrix (15.0 ± 3.1 nm; Figure S6, Supporting Information). The loss of size control and the presence of a residual matrix indicated that autonucleation from PTC was erratic, and that growth was primarily mediated through the amorphous intermediate phase.

3. One-pot nanoparticle synthesis using multivalent nucleating agents

The solvothermal synthesis of Co NPs with PTC as a growth agent was repeated using Co₁₆–calixarene **1** as an independent nucleation agent. Initial studies included oleic acid as a co-surfactant, based on our previous studies²⁹ and the reaction conditions above. However, the mean particle sizes were too small and the polydispersities were too large to meet our criteria for seeded growth with stoichiometric control. We attribute this to the effects of oleic acid on Co NP growth, including surface passivation,⁵³ suppression of decarbonylation,⁴³ and digestive ripening,⁴⁴ any of which can perturb NP nucleation and growth under thermal conditions.

To circumvent such complications, oleic acid was replaced with C11R, a less aggressive but highly effective surfactant for dispersing NPs in organic solvents.^{37,38} PTC and Co₁₆–calixarene **1** were dissolved in ODCB at Co mole ratios of 15 and 22, then heated with C11R for 60 min at 130 °C to produce Co NPs with size dispersities of 11–12% ($d = 12.6 \pm 1.6$ nm, 15.8 ± 1.8 nm). These NPs did not grow with further heating and remained enmeshed within the residual accretion (see below), but could be precipitated by EtOH and redispersed as chain-like aggregates (Figure 5a). High-resolution TEM and XRD analysis

indicated most Co NPs to be single crystals, with ϵ -Co as the predominant lattice phase (Figure 5b,c).^{54,55}

Thermal reactions at higher $[\text{Co}_{\text{final}}]/[\text{Co}_{\text{seed}}]$ ratios with C11R produced larger Co NPs, but the size distribution was broadened by the formation of smaller NPs, indicative of a competing nucleation pathway. To determine if secondary nucleation could be minimized by adjusting the reaction rate, the PTC solution was slowly fed into the reaction pot using a syringe pump following the initial growth phase at 130 °C, along with more C11R to maintain a constant surfactant concentration. An aliquot of the reaction mixture under slow-feed conditions was extracted at an intermediate stage and examined by TEM, which clearly revealed the presence of an amorphous accretion (Figure 6a,b). Elemental analysis by energy-filtered TEM imaging using electron-energy loss spectroscopy (EELS) confirmed high levels of Co within the accretion, in addition to C and O (Figure S7, Supporting Information). The accretion was gradually consumed upon further heating, to produce Co NPs up to 30 nm (Co mole ratio >100) with good control over particle size distribution and a strong correlation between $V_{\text{final}}/V_{\text{seed}}$ and $[\text{Co}_{\text{final}}]/[\text{Co}_{\text{seed}}]$ (Figure 6d). We note that the Co NP shapes became increasingly cubelike at higher Co mole ratios (further evidence of favorable conditions for nanocrystal growth), potentially skewing our volumetric analysis. NP size analysis based on edge lengths produced different mean volumes than those derived from the assumption of spherical NPs, but remained within range of the linear correlation.

4. Factors affecting accretive growth

The NP growth rate became sluggish at the highest $[\text{Co}_{\text{final}}]/[\text{Co}_{\text{seed}}]$ ratios, which resulted in substantial buildup of amorphous material on NP surfaces and compromised control over size dispersity (Figure 7a). The residual matrix was persistent in the presence of the mild surfactant C11R, but was readily digested upon treatment with oleic acid (Figure 7b). Dispersing the precipitate in a 10 mM solution of oleic acid in refluxing toluene resulted in fully dispersible Co NPs without the amorphous matrix, with minimal changes in particle size or shape. It is worth noting that Co NPs treated with oleic acid do not form dipole-directed assemblies such as rings or chains when deposited onto TEM grids from toluene solution, but exchanging the surfactant from oleic acid back to C11R resulted in their dipole-directed assembly and deposition as NP rings (Figure 7c).^{37,38} The utility of calixarenes for NP dispersion and self-assembly has been previously described.³⁹

Raising the temperature to 180 °C after injection of fresh PTC improved the growth rate but was not sufficient to dissipate the residual matrix. This suggested that (i) growth is transport-limited, with the accretion matrix acting as an interface between the growth monomer and the embedded NPs, and (ii) while the accretion is replenished by PTC addition, the network gradually becomes less permeable and hinders the diffusion of atoms and clusters to the NP surfaces, trapping a higher percentage of Co in the amorphous matrix. The net effect is a reduced efficiency in converting PTC into nanocrystalline Co. The buildup and permeability of this accretion is analogous to the development of physical barriers in other heterogeneous systems, such as the solid electrolyte interface (SEI) in Li-ion batteries.⁵⁶

To improve the efficiency of NP growth, we replaced C11R with a surfactant having sufficient activity to enable the migration of Co species and reduce buildup of the accretion

phase, yet mild enough to avoid autonucleation or digestive ripening of the Co NPs already formed. Previous studies by us have established that the properties of calixarene-based surfactants are strongly influenced by the chemistry of their macrocyclic headgroups.^{39,57} In this study, the best alternative identified was the octa-*O*-propargyl derivative of C11R (OP-C11R; Figure 8), whose pendant alkyne units could participate in ligand exchange reactions within the amorphous organocobalt network, but insufficiently reactive to digest the thermodynamically stable Co nanocrystals (for more details, see Supporting Information and Figure S8).

The seeded growth of Co NPs under slow-feed conditions was repeated by adding an ODCB solution of PTC (200 mM) and OP-C11R (4.8 mM) to a reaction pot with **1** at 180 °C ($[\text{Co}_{\text{seed}}] = 35 \mu\text{mol}$; see Experimental Section). TEM size analyses were performed by extracting aliquots from the reaction mixture at 1-hour intervals, corresponding with incremental changes in $[\text{Co}_{\text{final}}]/[\text{Co}_{\text{seed}}]$; Co mole ratios of 23, 46, 69, and 92 yielded Co NPs with mean diameters of 20.4 ± 2.0 nm, 28.0 ± 2.4 nm, 37.0 ± 3.4 nm, and 40.0 ± 4.4 nm, respectively (see Figure S9, Supporting Information). An excellent correlation was obtained when comparing Co NP volume against either growth time or Co mole ratio, in clear support of a seeded growth mechanism within the accretion (Figure 9). Again, the percentage of NPs with squarish cross sections increased at higher Co mole ratios, but the difference in mean values derived from cubic volumes was less than 10% relative to those based on the assumption of spherical NPs.

5. Accretive growth in the context of current nucleation and growth models

Mechanisms for the solution synthesis of NPs usually fall into one of the following categories: (i) rapid “burst” nucleation under supersaturation conditions followed by slower, diffusion-limited growth, as first described by LaMer and Dinegar;⁵⁸ (ii) slow, continuous nucleation in competition with fast, autocatalytic surface growth for the consumption of precursor, as described by Watzky and Finke;⁵⁹ (iii) secondary growth processes dominated by the aggregation of post-nucleation species, with a low barrier of recrystallization into single-domain NPs;^{60,61} (iv) size refocusing by thermodynamic mechanisms such as Ostwald or digestive ripening, whose rates can be adjusted by surfactant choice and concentration.^{15–17} With respect to the first two mechanisms, it is assumed that diffusion-limited NP growth takes place under ideal solution conditions. However, there are many reports in which inorganic NPs are formed within polymers and other organic matrices, such that nucleation and growth conditions are defined by the properties of the local embedding medium.^{27,28,62,63} In such situations, NP growth is likely to be determined by the rate at which the reactive species diffuses through the matrix. It is thus reasonable to consider additional mechanisms for NP growth that proceed through intermediate phases, rather than by the direct addition of growth monomers onto NP surfaces.

The continuous growth of crystalline Co NPs within the accretion matrix is noteworthy in several respects. First, unlike the classical burst nucleation mechanism,⁵⁸ the thermal decomposition of Co₁₆–calixarene **1** into capped-cluster intermediates does not depend on supersaturation, and the resulting nanoclusters are thermally stable and resistant to digestion or aggregative growth.²⁹ Second, the low autonucleation potential of PTC discourages

secondary cluster formation, permitting this reagent to contribute exclusively toward seeded growth following a nucleation event. This is congruent in some respects with the Watzky–Finke mechanism in which autocatalytic surface growth supersedes nucleation,⁵⁹ but involves distinct nucleation and growth agents. Third, the optimization of NP growth using slow-feed conditions indicates that the PTC monomer adds to the accretion mass rather than directly onto the Co NP surface. The efficiency of NP growth is not determined by solution kinetics, but rather by the mobility of Co species through the amorphous matrix, which in turn is defined by the activity of coordination ligands distributed throughout the network. In this study, mobility is sustained by the co-addition of polyvalent alkynes such as OP-C11R with growth monomer.

Previous studies on the nucleation and growth of metal NPs from carbonyl clusters or organometallic polymers have focused on the condensation of reactive species trapped within the medium, with the presumption that NPs are formed by the aggregation of smaller clusters within the confined spaces of the polymer matrix.^{27,28,62,63} In this context, NP growth is limited either by low reactant mobility or by stabilizing (capping) interactions with nearby polymer chains, with the latter offering opportunities to influence NP size and shape. In comparison, our studies suggest that Co NP growth with OP-C11R as the supporting surfactant is not hindered by the surrounding matrix: the polyvalent ligands have a dual role to stabilize the growing nuclei against aggregation, and to mediate the transport of Co species to NP surfaces through the accretion. In this fashion, NP size is essentially determined by the stoichiometry of nucleation and growth reagents, and the Co content within the accretion is effectively converted into crystalline NPs with low size polydispersity, which can then be released from the residual matrix by treatment with oleic acid. Lastly, we suggest that staged nucleation and growth according to the accretive model may have broader applicability in the synthesis of inorganic NPs, as exemplified by a recent study on the heterogeneous nucleation of PbSe nanocrystals within an intermediate amorphous phase.⁶⁴

Conclusions

Crystalline Co NPs can be formed with low size polydispersity within an amorphous accretion, formed by the condensation of Co₁₆–calixarene complex **1** and PTC. Thermal decomposition of **1** generates calixarene-stabilized nanoclusters, and growth within the amorphous matrix is mediated by mildly active surfactants such as OP-C11R, which permit the efficient migration of Co to the embedded NPs. The matrix can be fed with additional PTC to generate ϵ -Co NPs up to 40 nm, with linear increases in particle volumes as a function of added growth agent. The Co NPs are released from the residual matrix upon digestion with oleic acid, and can self-assemble into flux-closure rings when dispersed in toluene with C11R, aided by the enhanced dispersion properties of calixarene-based surfactants.³⁹

The intermediacy of an accretion matrix during NP growth is unlikely to be limited to cobalt, and may offer opportunities for new methods and reagents in the synthesis of other types of NPs. Areas for optimization include lower barriers for reactant mobility during accretive growth to increase NP size, and greater control over aggregation or secondary

nucleation processes to reduce polydispersity. In this regard, the inclusion of weakly coordinating surfactants within the accretion is likely important for establishing control over NP growth.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

Nucleation of Co nanoparticles using Co_{16} -calixarene **1**, followed by growth within an intermediate amorphous phase (accretion) that is fed by the addition of growth monomer (PTC).

Figure 2.

Co NPs prepared by the thermolysis of Co₁₆-calixarene **1** in the presence of C11R. (a) TEM images of Co NPs after heating **1** in ODCB for 20 min at 130 °C (*left*), then 1 h at 180 °C (*right*). (b) Size analyses of NPs produced at 130 °C (2.9 ± 0.4 nm) and 180 °C (3.6 ± 0.4 nm).

Figure 3.

(a) MALDI-MS of Co-calixarene complex **1** (DCTB matrix), with Gaussian distributions presented for major peak modes (green) and combined modes (red). The mode peaks correlate with oligomers of decarbonylated **1**; the average difference between the first 3 peaks (m/z) is 1880. (b) Expanded view of molecular ion signal, with m/z between fine peaks (marked with symbols) of 58–60, corresponding with successive loss of Co atoms. m/z between peak sets is 39, corresponding with loss of propargyl group.

Figure 4.

X-ray crystal structure of pentyne- $\text{Co}_4(\text{CO})_{10}$ (PTC). Two bridging μ -carbonyls shown in line-bond structure; the remaining eight CO ligands (two per Co atom) are hidden for clarity. For key bond lengths and angles, see Table S1 (Supporting Information).

Figure 5.

Growth of Co NPs using Co₁₆–calixarene **1** and PTC as nucleation and growth agents, respectively (Co mole ratio = 15). (a) Co NPs after growth ($t = 60$ min) and precipitation by EtOH ($d = 12.6 \pm 1.6$ nm). (c) HR-TEM image of single-crystal Co NPs. (d) XRD pattern of Co NPs; signals between $45\text{--}50^\circ$ correspond to the (221), (310), and (331) lattice peaks in the ϵ -phase.⁵⁵

Figure 6.

(a) Brightfield TEM image of Co NPs produced within an intermediate accretion, formed during PTC addition under slow-feed conditions following thermolysis of **1** at 130 °C. (b) Elemental Co map obtained by energy-filtered TEM analysis. (c) Co NPs produced after 3 hours of heating at 130 °C (Co mole ratio = 69; $d = 24.9 \pm 3.4$ nm). (d) Co NP diameter (○, left axis) and volume (●, right axis) as a function of Co mole ratio ($[\text{Co}_{\text{final}}]/[\text{Co}_{\text{seed}}]$; bottom axis) and reaction growth time (top axis), supporting stoichiometric control during particle growth. Error bars for Co NP diameters ($\sigma_{\text{rel}} = 11\text{--}15\%$) are based on TEM size analysis. An alternative volumetric analysis based on the edge lengths of cubic NPs was also applied in two cases (■, right axis).

Figure 7.

(a) Co NPs produced at a high $[Co_{final}]/[Co_{seed}]$ ratio (Co mole ratio = 119; $d = 28.8 \pm 4.5$ nm), trapped after growth within the residual accretion. (b) Fully dispersible Co NPs after treatment with oleic acid in toluene. (c) Deposition of Co NP ring, following surfactant exchange to C11R in toluene.

Figure 8.
Octa-*O*-propargyl C11 resorcinarene as an active component of the accretion matrix.

Figure 9.

Co NP diameters (○, left axis) and volumes (●, right axis) as a function of Co mole ratio and reaction time, produced by slow continuous addition of PTC and OP-C11R to Co₁₆-calixarene **1** in ODCB at 180 °C (also see Fig. S9, Supporting Information). The larger NP sizes per Co mole ratio indicate greater efficiency in growth. Error bars for NP diameters (RSD = 9–11%) based on TEM size analysis. An alternative volumetric analysis based on the edge lengths of cubic NPs ($N = 70$) was also applied in two cases (■, right axis).

Table 1

Size and volume increases using PTC for seeded growth

Initial size (nm) ^{a,b}	Final size (nm) ^{a,c}	Volume ratio (final:seed) ^d	Co mole ratio (final:seed)
4.5 ± 0.6	8.5 ± 0.8	6.7	4.4
4.7 ± 0.6	10.7 ± 1.0	11.8	7.8
4.5 ± 0.4	11.1 ± 1.6	15.0	14.7
4.7 ± 0.9	12.9 ± 1.6	23.6	28.4

^a Samples prepared for TEM analysis were previously exposed to air.

^b Pristine Co nanocrystals were produced by the thermolysis of Co₄(CO)₁₂ in ODCB with 20 mM oleic acid.

^c Growth conditions: 40 min at 130 °C in ODCB with 1 mM C11R.

^d A relative error (σ_{rel}) of 30% is assumed, based on data from TEM size analysis.