Prenucleation and coalescence of cobalt nanoclusters mediated by multivalent calixarene complexes†‡

Jie Liu and Alexander Wei*

Received (in Austin, TX, USA) 25th February 2009, Accepted 26th May 2009
First published as an Advance Article on the web 9th June 2009
DOI: 10.1039/b903954f

The formation of cobalt nanoclusters from polynuclear Co–alkyne species can be directed by multivalent calixarene ligands; thermochemical studies of Co_n–calixarenes reveal the influence of multivalency in prenucleation and postnuclear growth processes.

Inorganic and organometallic precursors for metal nanoparticle synthesis tend to be simple compounds, perhaps for practical reasons.[1] In most cases, the chemical information provided by supporting ligands is lost after the nucleation of precursors into nanoclusters, and are displaced by other surfactants or reactive species. The early loss of metal–ligand interactions imposes some limits on our ability to influence subsequent growth stages. For example, the metallization of organic nanostructures such as DNA is not conformal but proceeds stochastically with independent nucleation events along the chain, followed by coalescence into nanowires with roughnesses typically in excess of 5 nm.[2] Metal nanostructures have been "templated" within confined volumes, such as those supported by inverse micelles,[3] supramolecular gels or dendrimers,[4] biomolecular nanocapsules,[5] self-organized block copolymers,[6] and polymer brushes.[7] Most of these cases do not distinguish nucleation from growth processes, as nanoparticle formation is already dictated by the local metal concentration prior to reduction or heat activation.

In our interest to develop synthetic methods for novel magnetic nanostructures,[8] we considered whether kinetic growth processes before or after nucleation could be rationally influenced by a ligand-directed approach. In particular, multivalent ligands may serve as platforms for cluster formation but hinder postnucleation growth, resulting instead in the formation of nanoclusters by coalescence, as idealized in Fig. 1. This strategy depends on at least two criteria: (i) the coordinated species will readily decompose into precritical clusters upon thermal or chemical activation (prenucleation), and (ii) the metal–ligand interactions are sufficiently robust to maintain coordination, such that newly formed clusters would be stabilized by multivalent "caps." These capped clusters are expected to have lower reactivity yet are still capable of self-condensation into nanoclusters, but with stricter limits on postnuclear growth relative to more reactive (and less discriminate) monovalent precursors.

In this communication we examine the effect of multivalency on the kinetics of nanoparticle growth. Co nanoclusters are generated from Co_2–alkyne or Co_4–alkyne species, using the octapropargyl ether of C1 resorcinarene (**1**) or propargyl phenyl ether (PPE) as multivalent or monovalent ligands, respectively (Scheme 1). The thermal decomposition of metal carbonyls has been widely used in the synthesis of Co nanoparticles, but optimization of size and shape control is typically developed by experimenting with reaction conditions or surfactant stoichiometry.[9,10] While macrocyclic ligands have previously been employed in metal nanoparticle syntheses,[11] the results have been variable and not well correlated with nucleation or growth kinetics. To address this, we include a thermochemical analysis of organocobalt precursors to evaluate the effect of multivalency on thermal activation and postnucleation growth or ripening.

Octapropargyl ether **1** was prepared from tetramethylresorcinarene and treated with $Co_2(CO)_8$ or $Co_4(CO)_{12}$ to yield polynuclear Co–alkyne complexes **2** and **3**, respectively (Scheme 1; see ESI‡ for synthetic details). Addition of $Co_2(CO)_8$ or $Co_4(CO)_{12}$ to PPE yielded the monovalent Co_n–alkyne complexes **4** and **5**. In the case of polynuclear Co complex **2**, the formation of eight $Co_2(CO)_6$–alkyne units was confirmed by elemental analysis and X-ray crystallography§ (Fig. 2), by the disappearance of the C_{sp}–H stretch at 3280 cm^{-1} by IR spectroscopy, and by a migration in NMR chemical shift of the C_{sp}–H proton from 2.47 to 5.75 ppm.[12] The crystal structure of hexadecanuclear complex **2** shows all $Co_2(CO)_6$–alkyne units to be on the same face of the calixarene, and amenable to the prenucleation of zerovalent Co clusters.

In the case of polynuclear Co–calixarene complex **3**, elemental analysis indicates incomplete saturation with a mean of 5 Co_4 units per molecule. IR spectroscopy indicates a strong band centered at 1868 cm^{-1}, a signature peak for bridging CO ligands in Co_4–alkyne species,[13] as well as the absence of free alkynes. This suggests that one or more Co_4 clusters in **3** may be chelated by two propargyl ligands or possibly split into

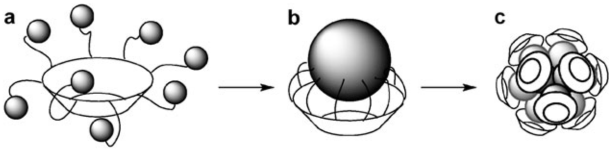
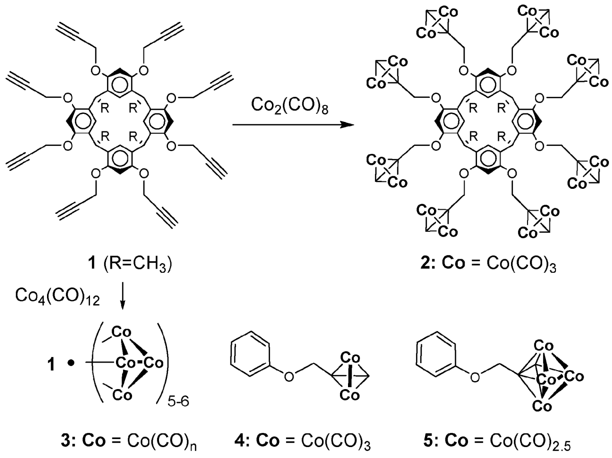


Fig. 1 (a) Multivalent metal–ligand complex; (b) prenucleation of capped cluster; (c) coalescence into nanocluster.

Purdue University, Department of Chemistry, West Lafayette, IN, USA. E-mail: alexwei@purdue.edu; Fax: +1 765 4940239; Tel: +1 765 4945257

† Dedicated to Professor Seiji Shinkai on the occasion of his 65th birthday.

‡ Electronic supplementary information (ESI) available: Synthesis and chemical characterization of **1–5**, conditions for thermogravimetric analysis and nanocluster synthesis, and particle size analyses for Fig. 5. CCDC 722503. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b903954f



Scheme 1 C1 resorcinarene octapropargyl ether **1**, Co-calixarene complexes **2** and **3**, and Co–PPE complexes **4** and **5**.

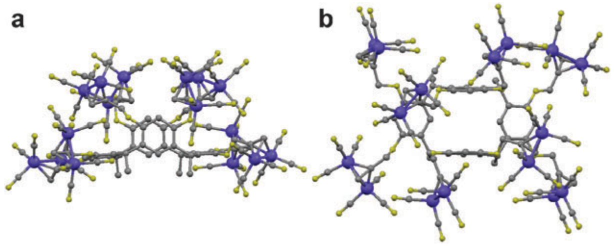


Fig. 2 X-Ray crystal structure of Co_{16}–calixarene complex **2**: (a) side view; (b) top view. For clarity, hydrogen atoms are omitted and cobalt atoms are enlarged. Co = violet; O = yellow.

Co_2–alkyne units. The literature does not indicate whether Co_4 carbonyl clusters can form stable complexes with multiple alkynes,[14,15] but cluster fission is known to occur with excess alkyne and diynes.[16]

Thermogravimetric analysis (TGA) of complexes **2–5** reveals significant differences with respect to thermal stability and multivalency (Fig. 3 and ESI‡). A comparison of Co_2–alkyne complexes (Fig. 3a and b) with Co_4–alkyne complexes (Fig. 3c and d) indicates an initially higher rate of decarbonylation for the former below 175 °C but a greater rate of weight loss for the latter at higher temperatures, in accordance with some earlier observations.[17] Furthermore, the thermal decomposition of multivalent Co_n–calixarenes **2** and **3** (Fig. 3a and c) is retarded relative to monovalent Co_n–PPE species **4** and **5** (Fig. 3b and d), requiring temperatures above 300 °C for complete decarbonylation.¶ We attribute this to differences in the stability of the surface ligands around the nascent Co clusters: monovalent PPE is prone to surface migration which contributes to autocatalytic decarbonylation,[10b,c] whereas the multivalent calixarenes are less mobile and present a barrier to metal polycondensation.

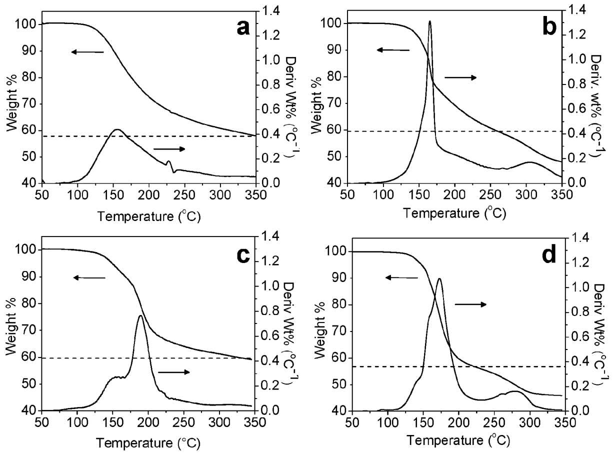


Fig. 3 TGA (relative weight loss and first derivative) of (a) Co_{16}–calixarene **2**, (b) Co_2–PPE **4**, (c) Co_n–calixarene **3** ($n \approx 20$), and (d) Co_4–PPE **5**. Weight loss corresponding to complete decarbonylation represented by dashed lines.

The effect of multivalency on the thermolysis of Co–alkyne complexes into Co nanoclusters was first evaluated by heating deaerated solutions of **2–5** in *o*-dichlorobenzene (ODCB) at a constant atom molarity ([Co] = 28 mmol), in the presence of oleic acid.‖ These solutions were maintained at reflux (182 °C) for at least 25 min to ensure complete consumption of the organocobalt precursors. Thermal decomposition occurred rapidly in all cases as indicated by the immediate blackening of the reaction mixture, but size analysis by transmission electron microscopy (TEM) indicated significant differences in particle size distributions (Fig. 4). The mean diameter of the nanoclusters generated from Co_{16}–calixarene **2** was 4.1 nm, whereas that produced from Co_2–PPE **4** at the same Co concentration was 6.3 nm (see ESI‡ for details). Similarly, the diameter of nanoclusters from Co_n–calixarene **3** ($n \approx 20$) was 6.5 nm, whereas that produced from Co_4–PPE **5** was 9.8 nm. Differences in particle size distributions from Co_2–alkyne *versus* Co_4–alkyne precursors (*i.e.* **2** *vs.* **3**, and **4** *vs.* **5**) were also observed. The larger particles from Co_4–alkyne species **3** and **5** correlate with their longer Co–C bonds and more efficient thermal decomposition.[17]

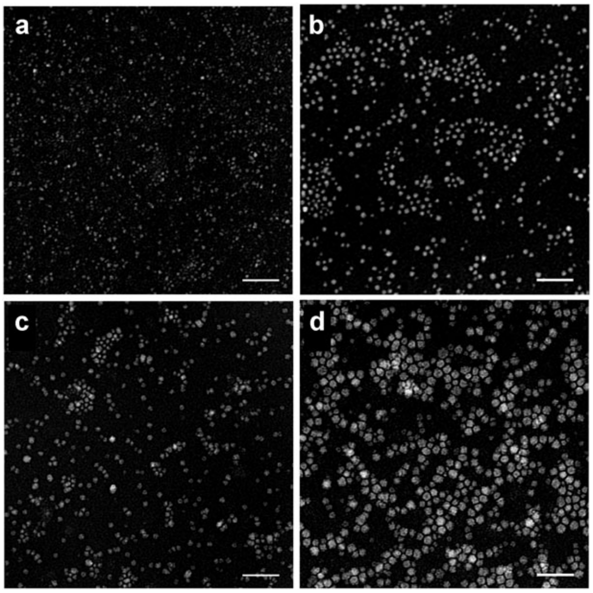


Fig. 4 TEM images (Philips CM-10, 80 kV) of metal nanoclusters produced by the thermolysis of Co–alkyne complexes in ODCB, using equal amounts of Co: (a) Co_{16}–calixarene **2** (4.1 ± 0.9 nm); (b) Co_2–PPE **4** (6.5 ± 1.0 nm); (c) Co_{20}–calixarene **3** (6.3 ± 1.0 nm); (d) Co_4–PPE **5** (9.8 ± 1.6 nm). Size analysis based on a minimum of 100 particles per image; scale bar = 50 nm.

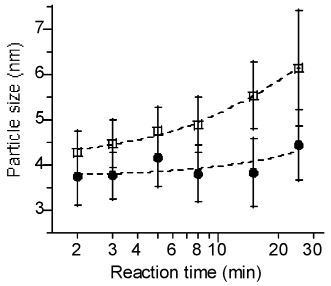


Fig. 5 Semilog plot of Co nanocluster sizes as a function of time, following rapid injection of Co_{16}–calixarene **2** (●) or Co_2–PPE **4** (☐) into hot ODCB ([Co] = 28 mmol). See ESI‡ for particle size analysis.

Rapid injection of Co–alkyne complexes into preheated ODCB solutions containing oleic acid‖ yielded Co nanoclusters with similar size distributions as above, and provided an opportunity to further examine the influence of ligand multivalency on particle size. Both Co_{16}–calixarene **2** and Co_2–PPE **4** yielded Co nanoclusters within the first 2 minutes after injection, but the initial size of the former was smaller and changed little over time, whereas the latter experienced significant postnuclear growth (Fig. 5 and ESI‡). The essentially invariant size of nanoclusters produced from **2** implies that calixarene **1** stabilizes the Co nanoclusters against Ostwald ripening and other postnucleation growth processes, in accordance with the TGA analysis.

The controlled thermochemistry of the multivalent Co–calixarene complexes suggests that their transformation into stable nanoclusters proceeds by prenucleation into metastable capped clusters, followed by coalescence. These results imply that calixarene **1** can also serve as a polyvalent ligand for Co surfaces, although further studies are needed to fully define the metal–adsorbate structure. Our comparative study with monovalent ligands demonstrates that multivalent species can influence the kinetics of nanocluster growth, both prior to and after the critical nucleation event.

The authors gratefully acknowledge the National Science Foundation (CHE-0243496) for financial support, Dr Philip Fanwick for X-ray crystallographic analysis, Dr Daniel Lee for microanalysis, and Clancy Kadrmas for assistance with thermogravimetric analysis.

Notes and references

§ X-Ray structural analysis (CCDC 722503) was performed using MoK_α radiation on a Nonius KappaCCD, equipped with a graphite crystal and incident beam monochromator.

¶ Additional mass loss for **4** and **5** (above 300 °C) is likely associated with PPE and its byproducts; see ref. 12 for examples.

‖ Oleic acid is widely used as a supporting surfactant in the synthesis of Co nanoparticles, and can assist the initial decarbonylation. The resulting nanoparticles are presumably passivated by a mixture of alkynes and carboxylates.

1 Y. Xia, Y. Xiong, B. Lim and S. E. Skrabalak, *Angew. Chem., Int. Ed.*, 2009, **48**, 60.

2 (*a*) E. Braun, Y. Eichen, U. Sivan and G. Ben-Yoseph, *Nature*, 1998, **391**, 775; (*b*) K. Keren, R. S. Berman and E. Braun, *Nano Lett.*, 2004, **4**, 323; (*c*) G. A. Burley, J. Gierlich, M. R. Mofid, H. Nir, S. Tal, Y. Eichen and T. Carell, *J. Am. Chem. Soc.*, 2006, **128**, 1398.

3 (*a*) M. Gobe, K. Kon-no, K. Kandori and A. Kitahara, *J. Colloid Interface Sci.*, 1983, **93**, 293; (*b*) S. H. Sun and C. B. Murray, *J. Appl. Phys.*, 1999, **85**, 4325; (*c*) C. Petit, A. Taleb and M. P. Pileni, *J. Phys. Chem. B*, 1999, **103**, 1805; (*d*) J. P. Wilcoxon, J. E. Martin and P. Provencio, *Langmuir*, 2000, **16**, 9912; (*e*) F. S. Diana, S.-H. Lee, P. M. Petroff and E. J. Kramer, *Nano Lett.*, 2003, **3**, 891.

4 (*a*) Y. H. Niu, L. K. Yeung and R. M. Crooks, *J. Am. Chem. Soc.*, 2001, **123**, 6840; (*b*) M.-K. Kim, Y.-M. Jeon, W. S. Jeon, H.-J. Kim, S. G. Hong, C. G. Park and K. Kim, *Chem. Commun.*, 2001, 667; (*c*) Y. Wang, J. Yang, Z. Zheng, M. D. Carducci, J. Jiao and S. Seraphin, *Angew. Chem., Int. Ed.*, 2001, **40**, 549; (*d*) C. S. Love, V. Chechik, D. K. Smith, K. Wilson, I. Ashworth and C. Brennan, *Chem. Commun.*, 2005, 1971.

5 (*a*) T. Douglas, D. P. E. Dickson, S. Betteridge, J. Charnock, C. D. Garner and S. Mann, *Science*, 1995, **269**, 54; (*b*) H. Yoshimura, *Colloids Surf., A*, 2006, **282–283**, 464.

6 (*a*) J. P. Spatz, T. Herzog, S. Mossmer, P. Ziemann and M. Möller, *Adv. Mater.*, 1999, **11**, 149; (*b*) T. Thurn-Albrecht, J. Schotter, G. A. Kästle, N. Emley, T. Shibauchi, L. Krusin-Elbaum, K. Guarini, C. T. Black, M. T. Tuominen and T. P. Russell, *Science*, 2000, **290**, 2126; (*c*) W. A. Lopes and H. M. Jaeger, *Nature*, 2001, **414**, 735; (*d*) L. A. Miinea, L. B. Sessions, K. D. Ericson, D. S. Glueck and R. G. Grubbs, *Macromolecules*, 2004, **37**, 8967.

7 O. Azzaroni, A. A. Brown, N. Cheng, A. Wei, A. M. Jonas and W. T. S. Huck, *J. Mater. Chem.*, 2007, **17**, 3433.

8 (*a*) S. L. Tripp, S. V. Pusztay, A. E. Ribbe and A. Wei, *J. Am. Chem. Soc.*, 2002, **124**, 7914; (*b*) S. L. Tripp, R. E. Dunin-Borkowski and A. Wei, *Angew. Chem., Int. Ed.*, 2003, **42**, 5591; (*c*) T. Kasama, R. E. Dunin-Borkowski, M. R. Scheinfein, S. L. Tripp, J. Liu and A. Wei, *Adv. Mater.*, 2008, **20**, 4248; (*d*) A. Wei, S. L. Tripp, J. Liu, T. Kasama and R. E. Dunin-Borkowski, *Supramol. Chem.*, 2009, **21**, 189.

9 (*a*) P. H. Hess and P. H. Parker, Jr, *J. Appl. Polym. Sci.*, 1966, **10**, 1915; (*b*) J. R. Thomas, *J. Appl. Phys.*, 1966, **37**, 2914; (*c*) D. P. Dinega and M. G. Bawendi, *Angew. Chem., Int. Ed.*, 1999, **38**, 1788; (*d*) V. F. Puntes, K. M. Krishnan and A. P. Alivisatos, *Science*, 2001, **291**, 2115; (*e*) V. F. Puntes, D. Zanchet, C. K. Erdonmez and A. P. Alivisatos, *J. Am. Chem. Soc.*, 2002, **124**, 12874; (*f*) H. Bönnemann, W. Brijoux, R. Brinkmann, N. Matoussevitch, N. Waldöfner, N. Palina and H. Mudrow, *Inorg. Chim. Acta*, 2003, **350**, 617.

10 (*a*) A. Lagunas, C. Jimeno, D. Font, L. Solà and M. A. Pericàs, *Langmuir*, 2006, **22**, 3823; (*b*) R. M. de Silva, V. Palshin, F. R. Fronczek, J. Hormes and C. S. S. R. Kumar, *J. Phys. Chem. C*, 2007, **111**, 10320; (*c*) R. M. de Silva, V. Palshin, K. M. N. d. Silver, L. L. Henry and C. S. S. R. Kumar, *J. Mater. Chem.*, 2008, **18**, 738.

11 (*a*) A. V. Nabok, T. Richardson, F. Davis and C. J. M. Stirling, *Langmuir*, 1997, **13**, 3198; (*b*) X.-M. Li, M. R. de Jong, K. Inoue, S. Shinkai, J. Huskens and D. N. Reinhoudt, *J. Mater. Chem.*, 2001, **11**, 1919; (*c*) J. Liu, J. Alvarez, W. Ong, E. Román and A. E. Kaifer, *Langmuir*, 2001, **17**, 6762; (*d*) J. Liu, W. Ong and A. E. Kaifer, *Langmuir*, 2002, **18**, 5981; (*e*) L. Li, X. Sun, Y. Yang, N. Guan and F. Zhang, *Chem.–Asian J.*, 2006, **1**, 664; (*f*) V. Huc and K. Pelzer, *J. Colloid Interface Sci.*, 2008, **318**, 1; (*g*) Y. Sun, C. G. Yan, Y. Yao, Y. Han and M. Shen, *Adv. Funct. Mater.*, 2008, **18**, 3981.

12 B. Happ, T. Bartik, C. Zucchi, M. C. Rossi, F. Ghelfi, G. Palyi, G. Varadi, G. Szalontai, I. T. Horvath, A. Chiesivilla and C. Guastini, *Organometallics*, 1995, **14**, 809.

13 G. Gervasio, R. Rossetti and P. L. Stanghellini, *Organometallics*, 1985, **4**, 1612.

14 M. J. Went, *Adv. Organomet. Chem.*, 1997, **41**, 69.

15 P. Chini and B. T. Heaton, *Top. Curr. Chem.*, Springer-Verlag, Berlin, 1977, vol. 71, pp. 3–70.

16 (*a*) K. Kruerke and W. Hubel, *Chem. Ber.*, 1961, **94**, 2829; (*b*) R. S. Dickson and G. R. Tailby, *Aust. J. Chem.*, 1969, **22**, 1143.

17 V. Calvo-Perez, A. Vega C, P. Cortes and E. Spodine, *Inorg. Chim. Acta*, 2002, **333**, 15.