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ScienceDirect
Coordination Chemistry Reviews 251 (2007) 1075–1100
COORDINATION CHEMISTRY REVIEWS
www.elsevier.com/locate/ccr

Review

Transition-metal nanocluster stabilization for catalysis: A critical review of ranking methods and putative stabilizers

Lisa Starkey Ott[1], Richard G. Finke*

Department of Chemistry, Colorado State University, Fort Collins, CO 80523, USA

Received 12 December 2005; accepted 21 August 2006
Available online 25 August 2006

Contents

Abstract

A significant problem in the burgeoning transition-metal nanocluster literature is the myriad of proposed, putative stabilizers. A main objective of the present contribution is to provide a critical review of the methods for, and current rankings of, claimed transition-metal nanocluster stabilizers, with a focus on catalytically active nanoclusters. Following a brief introduction to the literature methods for evaluating colloidal stabilizers (methods which are 41 and 105 years old), the need for modern methods to measure nanocluster stability via agglomeration kinetics is presented. Discussed

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* Corresponding author. Tel.: +1 970 491 2541; fax: +1 970 491 1801.
E-mail address: rfinke@lamar.colostate.edu (R.G. Finke).

[1] Prepared initially as the introductory literature review chapter for a PhD thesis, L. Starkey Ott, Colorado State University, August 2006.

doi:10.1016/j.ccr.2006.08.016

next is the one presently available method for evaluating additives (i.e., putative stabilizers) for the formation and stabilization of transition-metal nanoclusters, the so-called 5 criteria method; this is followed by a scheme presenting established nanocluster stabilization modes. Next, a table of 48 prototype examples of established and novel nanocluster stabilizers is presented, followed by a discussion of each stabilization mode with selected, representative examples. One conclusion of this review is that it is clear that reliable, quantitative studies ranking claimed nanocluster stabilizers, and understanding of how they work, are just now appearing. A second conclusion is that given the lack of quantitative methods to measure stability and thereby rank stabilizers, it follows that much of the information regarding nanocluster stabilization is not on firm ground. This first review of transition-metal nanocluster stabilizers is just the initial step towards achieving the overall goal of simplifying the "dizzying variety" of claimed nanocluster stabilizers into a preferred, small set of solvents and stabilizers en route to high stability, high catalytic activity nanoclusters.

Keywords: Methods for ranking nanocluster stabilizers; Transition-metal nanocluster stabilization modes; Transition-metal nanocluster formation mechanisms; DLVO theory; Transition-metal nanocluster agglomeration; The 5 criteria method; Nanocluster composition

1. Introduction to modern transition-metal nanoclusters

Transition metal nanoclusters are presently the focus of a great deal of scientific effort [1–5]. This focus derives in part from the sheer novelty of nanoclusters, plus the challenges of understanding their formation [6–8], stabilization [9–11], agglomeration [12], and size- and shape-dependent properties [13]. Nanoclusters also hold promise for several applications, including (but not limited to) catalysis [14–17] (including fuel cell catalysts [18]), quantum computers [19], photochemistry [20], optics [21], nanoelectronics [22,23], chemical sensors [24,25] and many others. In support of these claims, a recent book reviewing metal nanoclusters states, "Metal nanoparticles are certain to be the building blocks of the next generation of electronic, optoelectronic, and chemical sensing devices [26]." However, transition-metal nanoclusters remain only kinetically stable, the thermodynamic minimum being bulk metal in all cases to date. Consequently, substantial effort has been centered on *stabilizing* transition-metal nanoclusters, as long-term solution and solid-state (e.g., storage) stability is crucial if practical applications of metal nanoclusters are to be realized.

Modern transition metal nanoclusters are distinguished from traditional colloids by several important factors, initially summarized elsewhere [27]. Specifically, nanoclusters are expected to be smaller (1–10 nm) with near-monodisperse size distributions ($\leq 15\%$), while colloids are often >10 nm with much broader size distributions [27]. Additionally, modern nanoclusters should have reproducible syntheses leading to *compositionally well-defined*, isolable, and redissolvable nanoclusters [27]. In respect to these characteristics, classic colloids traditionally have less well-defined compositions (frequently, their surfaces are contaminated with oxide/hydroxide, water, and halides) along with less reproducible syntheses [28]. Modern nanoclusters are typically prepared in dried organic solvents, while traditional colloids (e.g., gold colloids [29]) were prepared in water. Many preparations of $Au(0)_n$ colloids in organic solvents now exist, however [30].

There are numerous methods used to prepare transition-metal nanoclusters; synthetic methods have been reviewed recently for the interested reader [4,5,18]. Briefly, there are two general approaches for the formation of metal nanoclusters: a "top-down" and a "bottom-up" approach. The "top-down" approach involves the thermal, chemical, or mechanical [31–34] decomposition of a larger metal structure (typically either a metal powder [31] or a metal target [32–34]) into metal colloids or nanoclusters. For example, Klabunde et al. pioneered a top-down method of deposition of vaporized metal atoms from a solid metal source for the formation of weakly solvated transition-metal nanoclusters; this method, however, yields little size or compositional control [35–37]. The more common "bottom-up" approach involves generating the nanocluster by decomposition (usually reduction) of an organometallic precursor. A common preparation method involves reducing metal salts with a suitable reductant such as hydrogen gas or BH_4^- to form neutral $M(0)_n$ nanoclusters [18]. Some additional nanocluster synthesis methods include electrochemical reduction [38,39] or sonochemical decomposition of organometallic precursors [40,41]. Nanocluster *formation* and then *stabilization* are tightly interlinked issues as will become clear in what follows.[2]

2. Past and present methods for ranking the efficacy of nanocluster stabilizers

The stability of colloids has been of interest to researchers for over a century [42]. Most of the earlier work attempting to measure colloidal stability was performed on Au colloids, which have been known since the time of Faraday [43]. In 1901, the stability of Au colloids was studied as a function of added stabilizing agents including glues, gums, and starches [42]. In that work, Zsigmondy established the "gold number", the weight of an added protecting agent that is just incapable of preventing the agglomeration of 10 mL of a gold colloid within 3 min after the addition of 1 mL of 10% NaCl [42]. However, in the intervening 105 years, this method of assaying colloidal stability has had very little application; it is also of little relevance to metals

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[2] For instance, recent work on the preparation of stable $Pt(0)_n$ nanoclusters showed that what was thought to be a *stabilization* issue was in fact a *formation* issue [7]. In that work, ca. 100 experiments done under non-optimum, non-mechanism-based conditions yielded bulk metal. However, knowledge of the four-step mechanism (vide infra) of nanocluster formation and agglomeration, application of optimized synthetic conditions, and a key solvent change from the low dielectric constant solvent acetone to the high dielectric constant solvent propylene carbonate led to the formation of stable, 4.0 ± 1.0 nm $Pt(0)_n$ nanoclusters. Without the application of the mechanistically predicted [7,8] synthesis conditions and the change to propylene carbonate during the *formation* of the nanoclusters, *stabilization* of $Pt(0)_n$ nanoclusters in the absence of bulk metal proved impossible. This is just one example illustrative of the fact that nanocluster formation and stabilization are tightly interlinked issues.

other than gold and/or colloids prepared in solvents other than water—that is, to almost all modern transition-metal nanoclusters. Additionally, ill-defined colloidal protecting agents such as glues, gums, and starches are not currently employed, nor desired, for modern transition-metal nanoclusters where determining the composition of the resultant nanocluster is one key to understanding their stability [14]—a little accomplished key, as we shall see.

A somewhat more recent, but still 41-year old, 1965 study also examined the stability and aggregation of Au colloids, this time by defining "protective value" as "the number of grams of a gold sol which are just protected by 1 g of the protective agent against flocculation by 1% NaCl solution [44]." The protective value was evaluated for 22 protecting agents, and the authors concluded that gelatin and poly(acrylic acid hydrazine) were the most effective at preventing agglomeration for Au colloids. However, the results of this study are difficult to interpret because colloidal stability was studied at different temperatures and for varying amounts of time. Consequently, the stabilizers examined therein [44] should not be rigorously compared either to each other or to prior stabilizers. Like the gold number study discussed above [42], the protective value study has little relevance to colloids of metals other than Au prepared in solvents other than water. Accordingly, the "protective value" is cited mainly either as precedent for stabilizing nanoclusters with polymers [45,46], or as interesting "history" in the literature of modern transition-metal nanoclusters [7,9].

Note, then, that these two, >105 and >41-year old methods available in the literature for ranking nanocluster stabilizers have been used *only* used for *Au colloids* and are applicable *only* in *water*. Additionally, these two methods rely on *visual inspection* of a solution (i.e., the color change from red to violet with the agglomeration of the Au colloids) in order to determine the efficacy of the stabilizer. Clearly, these water-soluble, Au colloid-based, qualitative methods are not the desired quantitative method for ranking stabilizers of all metal nanoclusters in a range of solvents. New methods are needed to quantitatively rank nanocluster stabilizers, and have been under development since in our labs 2002 [9,12]. In addition, new methods of preparing Au colloids in organic solvents with only the desired stabilizer(s) and solvent present would presumably open up optical methods of following nanocluster stabilization; such methods are also under consideration [47].

2.1. *Agglomeration-based methods of determining nanocluster stability*

In a classic study, Enüstün and Turkevich studied preformed citrate-stabilized Au colloids and the kinetics of their $NaClO_4$-induced agglomeration [48]. Aliquots of the colloids were taken at predetermined times after the addition of $NaClO_4$, and agglomeration was halted via the addition of a 0.1% gelatin solution. Transmission electron microscopy (TEM) was employed to measure agglomeration. While a valuable, classic study, this paper relies solely on TEM for studying the stability of the colloids. TEM is a useful tool for studying agglomeration, but complications under the harsh conditions of the electron beam include: aggregation [49], charging of the solvent in the electron beam [50], and even nanocluster formation under the TEM beam from nanocluster precursors of especially first row metals [49,51,52]. Additionally, as noted in a TEM textbook, "Certain materials are more susceptible than others, but in the end, you can damage virtually anything you put into the TEM [53]." In short, TEM is an *ex situ* tool and thus not the desired, *in situ/operando* method for studying nanocluster agglomeration.

An alternative and potentially powerful technique for studying the formation and then agglomeration of nanoclusters over time is ultraviolet-visible (UV–vis) spectroscopy. This technique is dependent on (i) the precursor having a measurable absorbance, (ii) the nanocluster having a plasmon absorbance band measurably shifted from the precursor's absorbance band, and (iii) both of these absorbances being in the range of 160–780 nm. UV–vis spectroscopy can be valuable if all three of the above conditions are met, and has yielded information about the timescale of precursor degradation, colloid formation, and subsequent colloidal agglomeration [54,55]. However, the limitations imposed by the necessity of a plasmon absorbance band, preferably in the visible region (i.e., a band which does not just tail off into the UV), limits the utility of this technique to primarily Au, Ag, and Cu. Confirming the limited utility of a UV-vis method is Mie theory [56], which serves as an accurate predictor of the extinction spectra for a variety of colloids. Creighton et al. have calculated the absorption spectra for 52 metallic colloids [57] and their results show that nanoclusters of several of the important transition metals in nanocluster science (e.g., Ir, Rh, Ru, Pd, and Pt) have little absorbance in the visible region. Instead, they tail into the UV, making quantitation of nanocluster formation and agglomeration of such metals largely unaccomplished – at least to date – by this otherwise promising physical method [29,58,59].

Another method used to study the agglomeration of nanoclusters is dynamic light scattering (DLS). DLS appears to be a promising technique for following formation and agglomeration, as measurements can be taken *in situ* and in real time versus the extent of the reaction. However, measuring nanocluster formation and agglomeration with DLS is fraught with difficulty and its use is contentious at present [60,61]. For instance, the possibility of multiple scattering of particles [60,61] is a challenge, and polydisperse samples complicate the interpretation of the data [62]. Also, deconvoluting particle sizes from a single autocorrelation function (as in light scattering experiments) is a classic problem in curve fitting of multiple exponentials [63]. Additionally, the use of DLS in studying agglomeration is restricted to relatively small particles that have appreciable Brownian motion [64]. Hence, employing DLS for studying transition-metal nanoparticle agglomeration is not yet widespread.

One recent report details the use of a commercial high-performance particle sizer (HPPS), a modified version of traditional DLS instrumentation, for studying nanocluster formation and agglomeration [65]. The authors claim that this instrument offers a high sensitivity, rapid, relatively inexpensive method for studying the *in situ* formation (and agglomeration) of colloids. However, for the discrete "football" shaped polyoxoanion nanoparticle $P_2W_{18}O_{62}{}^{6-}$ (which is ~1.2 nm × 1.5 nm), the instrument detected only the long axis [65]. Additionally, HPPS presumably cannot measure the kinetics of the loss of monometallic nanocluster precursors. Moreover, it appears that this instrument is not useful in at least its reported configuration for reactions with gaseous reagents, such as the common reductant H_2. In short, at present there is no *quantitative* kinetic measurement of the conversion of precursor to nanocluster or nanocluster to agglomerated material using HPPS.

Other scattering techniques for monitoring nanocluster nucleation, growth, and agglomeration have also been used; the two that appear most promising at present are X-ray absorption fine structure (XAFS) spectroscopy and small angle X-ray scattering (SAXS) spectroscopy [66–71]. Both XAFS and SAXS can yield the highly desirable measurement of nanocluster formation and agglomeration *in situ*, allowing for the real-time monitoring of the kinetics. Furthermore, SAXS can sometimes be used to determine the molecular weight (MW) of nanoclusters [66]. For just one example, XAFS spectroscopy was used to determine that the dehydrogenation catalyst derived from $[(1,5\text{-COD})RhCl]_2$ is a Rh_6 species[3] [72]. Separately, a recent study compared SAXS with the *ex situ* size characterization techniques TEM and X-ray diffraction (XRD) for the measurement of $CoPt_3$ particle size distributions. This study found that all three techniques were within error for determining nanocluster size – however, SAXS offered the key benefits of an *in situ* approach and a much larger (i.e., and is thus more representative) sample size than TEM [68]. Currently, the main drawbacks of these techniques are their availability: XAFS requires a synchrotron radiation source, while both XAFS and SAXS require and the use of a highly specialized reaction apparatus (for example, for typical transmission-mode SAXS measurements, the reaction cell must have a pathlength of $\leq$1 mm). Nevertheless, broader use of these promising techniques should yield more accurate information on the formation and agglomeration of nanoclusters.

However, at present none of the TEM, UV–vis, DLS/HPPS, XAFS, or SAXS methods outlined above currently offers a readily available, quantitative method for evaluating agglomeration and stability.[4] Additionally, it is rare [68] for a study to use more the one technique to assay stability: a survey of the literature reveals that a "typical" nanocluster paper often reports stability only through the observation of nanoclusters or colloids *by TEM*. If nanoclusters are seen in the *solid state* by TEM, even if agglomerated and if the state of the remainder of the sample is unknown (i.e., there might be some or even primarily bulk metal present), the nanoclusters are typically deemed "stable". Hence, developing a quantitative method for following the agglomeration kinetics of transition-metal nanoclusters in solution is of enormous fundamental as well as practical importance. New methods for evaluating nanocluster stability promise to significantly advance the synthesis, isolation, and stability/storage properties of transition-metal nanoclusters.

2.2. *Can the catalytic reporter reaction method measure the kinetics of agglomeration?*

It is clear that a quantitative method for ranking nanocluster stabilizers is needed. To this end, *kinetic* measurements of agglomeration[5,6] are most desirable, for example using the established agglomeration-inducing ligand pyridine [62,73]. However, kinetic probes of agglomeration are relatively rare [6–8,12]. One kinetic method that has been successfully applied to follow the nucleation and growth of transition-metal nanoclusters [6,14,74] is the cyclohexene hydrogenation catalytic reporter reaction method. The reporter reaction as used in the two-step, autocatalytic nanocluster formation reaction discovered and developed by the Finke research group [6,14,74] is shown below in Scheme 1.

The cyclohexene reporter reaction method allows an indirect but rapid, quantitative, and real-time monitoring of the kinetics of nanocluster nucleation and growth and (in principle) agglomeration, vide infra. The cyclohexene hydrogenation must be much faster than the nanocluster formation to accurately amplify the kinetics of nanocluster nucleation and growth. Use of the cyclohexene reporter reaction has been well documented for following the two-step nanocluster nucleation and growth mechanism [6,14,74].

In order to quantify nanocluster stability, kinetic methods monitoring nanocluster nucleation, growth, and *agglomera-*

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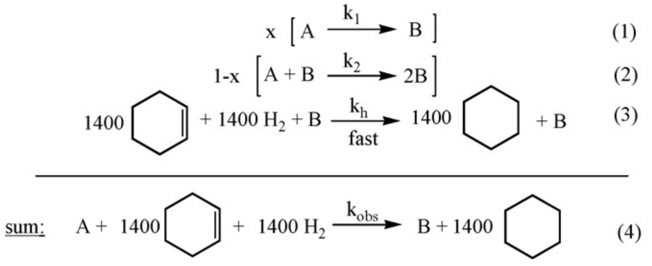
[3] In recent work at Pacific Northwest National Laboratories (PNNL), the $[Rh_6(\text{unknown stabilizer})]^{n+/0/n-}$ sub-nanometer cluster initially detected by XAFS and XANES [72] is now hypothesized to be a (perhaps more general) "Rh_4" cluster (J.C. Linehan, T. Autrey, J. Fulton, private communication). Collaborative studies are in progress to determine (i) the full composition of the cluster; (ii) whether or not it is the true catalyst vs. a catalyst resting state or catalyst precursor; and (iii) the broader generality or not of the "M_4" sub-nanocluster finding: J.C. Linehan, T. Autrey, J. Fulton, R.G. Finke, experiments in progress.

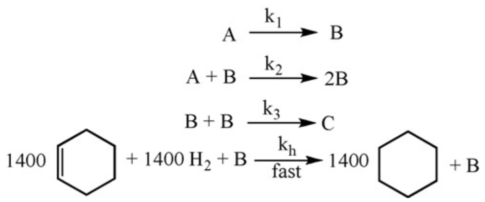
[4] Additionally, there is a little-cited "Fuch's Stability Ratio", W (see, for the only colloidal/nanocluster text of eight searched which contained a description, S. Ross, I.D. Morrison, *Colloidal Systems and Interfaces*, Wiley-Interscience, New York, 1988; for the original work describing the stability ratio, see: N Fuchs, Z.Phys 89 (1934) 736). W is obtained by measuring the $t_{1/2}$ of nanocluster agglomeration, which is presumably measuring the $B + B \rightarrow C$ and $B + C \rightarrow 1.5C$ steps of nanocluster agglomeration (see Section 2.2). One reason why Fuch's Stability Ratio is little reported/measured is that that colloidal/nanocluster agglomeration kinetics are very difficult to measure, vide supra.

[5] Difficulties studying nanocluster agglomeration directly reflect its inherent complexity, as stated in a recent review: "Aggregation in most real systems involves a wide range of physical and chemical processes including long- and short-range interactions (van der Waals forces, screened electrostatic interactions, steric effects, hydrodynamic interactions, etc.), adsorption and desorption of ions and neutral species, chemical bond formation, sintering, bridging, etc. In addition, a variety of processes can occur during and after aggregation. These include structural reorganization, reversible aggregation, and chemical processes. In addition, many aggregation processes involve particles with a broad range of sizes, shapes, and compositions. The aggregating particles may also have a surface geometry and large heterogeneities in their surface chemistry. It is clear that incorporation of all these (and many other) effects (such as the change in the solvent structure near to the particle surface) in a single model would be a *formidable undertaking*." (italics have been added) P. Meakin, Adv. Coll. Int. Sci. 28 (1988) 249.

[6] Agglomeration and aggregation are used synonymously in the literature, as they will be in this text. Herein, we use these words to describe irreversible chemical bond formation between one or more clusters, leading eventually to the formation of larger, eventually bulk-type metal.



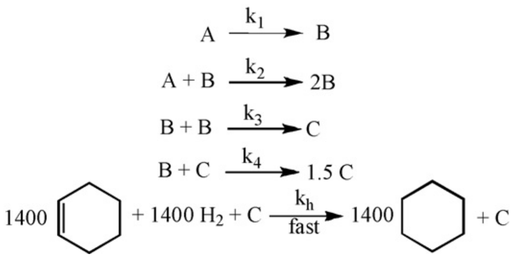
Scheme 1. The generalized two-step nanocluster formation reaction mechanism and associated rate constants k_1 and k_2. In this scheme, **A** is the organometallic precursor and **B** is a catalytically active atom on the surface of the nanocluster. The reaction is monitored by the fast cyclohexene reporter reaction (3). The sum reaction (4), is a so-called pseudoelementary step as discussed elsewhere [6,74].



Scheme 2. The three-step mechanism for nanocluster nucleation, surface autocatalytic growth, and bimolecular agglomeration. **A** and **B** are the same species as back in Scheme 1; **C** is inactive, agglomerated **B** in *this* three-step mechanism.

tion are necessary and have recently been developed [7,8,12]. Two mechanisms have been elucidated, the first being a three-step mechanism describing nanocluster nucleation, growth, and agglomeration where the catalytically *active* species is the nanocluster, **B**, and the agglomerated material, **C**, is catalytically *in*active [7], Scheme 2. The three-step mechanism follows nanocluster nucleation (rate constant k_1), growth (rate constant k_2) and agglomeration (rate constant k_3) using the cyclohexene reporter-reaction method to amplify the kinetics of formation and agglomeration of nanoclusters [6,14,74]. For example, the three-step mechanism is able to monitor the nucleation, growth, and agglomeration of $P_2W_{15}Nb_3O_{62}{}^{9-}$- and Bu_4N^+-stabilized $Ir(0)_n$ nanoclusters in acetone solvent with two added equivalents of the known nanocluster agglomerant, pyridine [12].

A four-step, and thus an overall new, believed to be more general [7,8] mechanism for nanocluster growth and agglomeration has also been recently described, Scheme 3 [7,8]. The four-step mechanism includes an *autocatalytic* agglomeration step, $\mathbf{B} + \mathbf{C} \rightarrow 1.5\mathbf{C}$ (where, as in Scheme 2, **B** is a nanocluster and **C** is agglomerated, bulk-type metal) [7,8]; a more graphic, pictorial representation of this mechanism and of[7] **A**, **B**, and **C** is available elsewhere for the interested reader [7,8]. In the four-step mechanism, weakly stabilized nanoclusters aggregate to form what is presently thought to be bulk-type metal, **C**, which serves as the catalytically active species (for cyclohexene hydrogenation) due to a ligand-poisoning effect especially in the smaller nanoclusters, **B** [7,8]. In addition, and of potentially special significance in developing a quantitative measure of nanocluster stability, is that *the four-step mechanism defines for the first time the two rate constants for agglomeration, k_3 and k_4, that one needs to measure to assay nanocluster stability*.



Scheme 3. The four-step mechanism for nanocluster formation and agglomeration. Herein, the nanocluster **B** is catalytically *inactive* while **C** is the active catalyst. Note that the overall mechanism contains two autocatalytic steps, $\mathbf{A} + \mathbf{B} \rightarrow 2\mathbf{B}$ and $\mathbf{B} + \mathbf{C} \rightarrow 1.5\mathbf{C}$.

With respect to quantitating agglomeration kinetics and, hence, stability, it has recently shown that one can induce the four-step mechanism of formation and agglomeration for prototype $P_2W_{15}Nb_3O_{62}{}^{9-}$-stabilized $Ir(0)_n$ nanoclusters beginning with the organometallic nanocluster precursor $[Bu_4N]_5Na_3[(1,5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}]$ and 44 equiv. of added pyridine [75]. However, with ≥50 equiv. added pyridine, the cyclohexene reporter reaction is poisoned and the catalytic reporter reaction method cannot be used to quantify the agglomeration kinetics. We have also observed the same results beginning with preformed, isolated, and redispersed $P_2W_{15}Nb_3O_{62}{}^{9-}$-stabilized $Ir(0)_n$ nanoclusters: ≥20 equiv. added pyridine poisons the cyclohexene reporter reaction. Hence, using added pyridine to induce and subsequently quantify the agglomeration kinetics for the four-step mechanism has not proven useful [75].

However, and importantly, it has proven possible to quantify the agglomeration kinetics using the temperature-induced agglomeration of preformed, isolated, and redispersed $P_2W_{15}Nb_3O_{62}{}^{9-}$ – stabilized $Ir(0)_n$ nanoclusters [75]. The rate constants k_3 (for $\mathbf{B} + \mathbf{B} \rightarrow \mathbf{C}$) k_4 (for $\mathbf{B} + \mathbf{C} \rightarrow 1.5\mathbf{C}$) were measured from 10 to 50 °C, allowing the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for each of the two steps to be determined: $\Delta H_3^{\ddagger} = 6.2(3)$ kcal/mol and $\Delta S_3^{\ddagger} = -46(2)$ eu and $\Delta H_4^{\ddagger} = 18(1)$ kcal/mol and $\Delta S_4^{\ddagger} = -2.5(2)$ eu. The magnitude of the $\Delta H_3^{\ddagger}$ and $\Delta S_3^{\ddagger}$ values suggest that $\mathbf{B} + \mathbf{B} \rightarrow \mathbf{C}$ proceeds via an *associative* mechanism [76,77]—that is, the nanoclusters agglomerate before the $P_2W_{15}Nb_3O_{62}{}^{9-}$ ligand dissociates from the surface(s). Conversely, the magnitude of the $\Delta H_4^{\ddagger}$ and $\Delta S_4^{\ddagger}$ values suggest that $\mathbf{B} + \mathbf{C} \rightarrow 1.5\mathbf{C}$ proceeds via a *dissociative* mechanism, with $P_2W_{15}Nb_3O_{62}{}^{9-}$ leaving the surface(s) before the particles agglomerate. Note that these mechanisms confirm our previous finding that metal-ligand bond energies can be up to two-fold stronger in nanoparticles (**B**, leading to a associative mechanism) than in the corresponding bulk metal (**C**, leading to a dissociative mechanism) [7,8]. These temperature-induced agglomeration experiments represent, to the best of our knowledge, the first experimental, quantitative measurement of

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[7] In fact, the true size, ligands, and other nature of **B** and **C** remain to be fully understood. Studies using XAFS, XANES, SAXS and other appropriate methods are in progress.

modern transition-metal nanocluster agglomeration [75]. This initial report [75] opens the door for future kinetic, quantitative measurements of nanocluster stability, at least for systems that are stable enough to be isolable and redissolvable. Interesting, historically, in this regard is Turkevich's statement in his 1963 classic on the "Coagulation of Colloidal Gold" [48] in which he notes that studies of agglomeration/coagulation in the early days of colloid chemistry were important in providing evidence as to the very existence of the colloidal state [48].

2.3. The 5 criteria method for evaluating both the formation and stabilization of modern, catalytically active transition-metal nanoclusters

A 2002 paper reported the development of a method for evaluating both the *formation* and *stabilization* of catalytically active[8] transition-metal nanoclusters [9]. This method relies on five criteria for ranking each stabilizer; hence, it is called the 5 criteria method. Its use initially focused on evaluating anionic stabilizers, as anions are known to be key [78] in DLVO-type stabilization (named after its founders Derjaugin, Landau, Verwey, and Overbeek; this and other modes of nanocluster stabilization will be discussed more in a moment). Briefly, the five criteria are: (i) a high level of kinetic control during the nanocluster formation reaction, as reflected by a large value of the k_2/k_1 ratio for autocatalytic growth (k_2) to nucleation (k_1), see Scheme 1; (ii) the formation of near-monodisperse nanoclusters (by definition elsewhere [27], nanoclusters with a size distribution of $\leq$15%) as verified by TEM; (iii) the ability to isolate from solution and bottle, without bulk metal formation, the nanoclusters for future use; (iv) the catalytic activity of the redissolved (i.e., from previously isolated) nanoclusters in a chosen solvent with fresh catalytic substrate (typically cyclohexene); and (v) the total turnovers (TTOs) for cyclohexene hydrogenation observed for *in situ* generated nanoclusters in solution. The combination of the above five criteria provides a previously unavailable evaluation of a chosen additive's ability to allow the formation, stabilization, and subsequent catalytic activity of transition-metal nanoclusters, one not limited to only those nanoclusters that are stable enough to be isolated and redissolved. Additionally, the 5 criteria method is applicable at least in principle to all metals in a range of solvents. The method and five criteria, while clearly not perfect[9]—for example, the method lacks the desired kinetic measurements of the two types of agglomeration (k_3 and k_4), so that a "7 criteria method" is desirable and under development—are nevertheless a welcome advance in an area where modern methods to rank nanocluster stabilizers were previously totally lacking.

The Best Anions for the Formation and Stabilization of Ir(0) Nanoclusters in Acetone at 22 °C:
$[P_2W_{15}Nb_3O_{62}]^{9-} \sim [(P_2W_{15}Nb_3O_{61})_2O]^{16-} \sim$
$\{[P_2W_{15}(TiOH)_3O_{59}]^{9-}\}_n$ (n=1,2) $> [SiW_9Nb_3O_{40}]^{7-} >$
$HPO_4^{2-} > H_2PO_4^{-} > [C_6H_5O_7]^{3-}$

Poorer Anions for the Formation and Stabilization of Ir(0) Nanoclusters:
$[P_3O_9]^{3-} > [\text{-}CH_2\text{-}CH_2(CO_2)\text{-}]_n^{n-} > Cl^- > OH^-$

Scheme 4. The anion stabilization series first reported elsewhere [11].

Initially, the five criteria have been used to rank established anionic nanocluster stabilizers, leading to the first anion stabilization ability series for $Ir(0)_n$ nanoclusters, Scheme 4 [9]. Use of a balanced reaction stoichiometry plus the five criteria also led to the insight that Proton Sponge^{TM} (PS^{TM}; 1,8-bis(dimethylamino)naphthalene) is an effective scavenger for the H^+ product of nanocluster formation reaction when H_2 is the reductant [10]. Hence, PS^{TM} is an important component of nanocluster formation and stabilization studies using H_2 as the reductant [10,11].

Insights from the 5 criteria method also led to the development of a "lattice-matching model" [79] that provides an important, molecular-level hypothesis for how tridentate anionic stabilizers may achieve their higher observed level of stabilization, a *hypothesis* useful for predicting which anions are effective for coordinating the M(1 1 1) face of a metal nanocluster [79]. The essence of that model is that the best anionic nanocluster stabilizers present a tridentate, facial array of oxygen atoms for coordination to selected $M(0)_n$ surfaces, and that the preferred tridentate oxoanion stabilizers are those that have the best match between the ligand O–O and metal M–M distances. In addition, the lattice matching model and the 5 criteria have recently been used to predict, then verify, a previously unappreciated nanocluster stabilizer, HPO_4^{2-} [11]. The important result is that HPO_4^{2-} is a simple, effective, readily available, and robust stabilizer for at least $Ir(0)_n$ nanoclusters, and probably nanoclusters of other metals such as Rh, Pt, Au, and Cu for the reasons detailed elsewhere [79].

In short, the 5 criteria method has been a valuable development in assaying both nanocluster formation and stabilization. It is the lone method currently available in the literature that is applicable, at least in principle, to all transition metal nanoclusters in a range of solvents. However, a weakness of the method is that for less stabilized systems where bulk metal is readily formed, four of the five criteria become unavailable (however, the fact that four of the five criteria become unavailable in itself is helpful, as it indicates which stabilizers are even *worth ranking*). Overall, the 5 criteria method is an important advance in both understanding the factors controlling nanocluster formation and stabilization and in ranking stabilizer efficacy. Eventually, improved methods in measuring both the k_1 and k_2 rate constants for formation and k_3 and k_4 rate constants for agglomeration simultaneously (Scheme 3, vide supra) as part of the 5 criteria method should allow refinements in the initial rankings made with the 5 criteria method, en route to a preferred, 7 criteria method.

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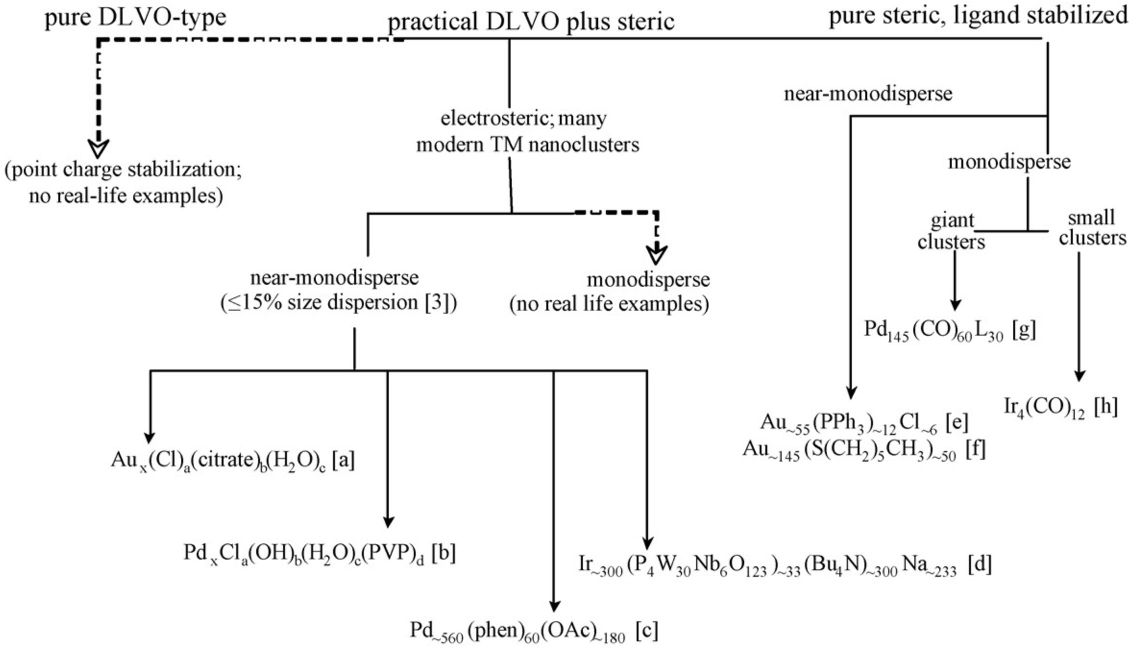
[8] Often, an inverse correlation between high stability and high catalytic activity is observed [8] – not unexpected, as highly stable nanoclusters often have a large fraction of their otherwise catalytically active surface sites ligated by the stabilizer, Scheme 5. Thus, a *balance* between stability and catalytic activity is key in achieving optimum nanocluster catalysis [14–17].

[9] In cases where bulk metal is formed, 4 of the 5 criteria become unavailable, so that the 5 criteria method is applicable in practice only to fairly well-stabilized nanoclusters.

3. On the modes of nanocluster stabilization

There are two established classes of nanoclusters stabilizers: (i) electrostatic (also known as electronic, or DLVO-type) and (ii) steric stabilizers. Representative examples are shown in Scheme 5. A third type of nanocluster stabilization, which is frequently presented in the literature but has not been defined precisely in terms of both overall stabilizer size and charge requirements [80], is "electrosteric" stabilization (a combination of electrostatic and steric; it is included in Scheme 5 and will be discussed critically later, in Section 3.3). These three modes of stabilization will be discussed in separate sections below, and then three additional examples of "non-historical" putative stabilization modes will also be discussed after that, cation-only, solvent-only, and ionic liquid stabilization. *Note that given the previously discussed lack of quantitative methods to measure stability and thereby rank stabilizers, it follows that much of the information that follows is not on as firm a ground as is desired.* Nevertheless, it is useful if not necessary to critically review what is known or believed to be true. Note also is that we unavoidably run into problems of nomenclature [27], and a lack of sufficient data: we want stabilization data for compositionally and otherwise well characterized *nanoclusters*, but most of what is available are data for compositionally ill-defined *colloids* (see the definitions and distinctions elsewhere between nanoclusters and colloids [27]).

A general word of caution is necessary before beginning a discussion on the modes of nanocluster stabilization. When evaluating a system, the source of stabilization may seem clear: for example, a coordinating anion or polymer may be present. However, in many systems, there are often multiple possible stabilizers present so that one must carefully consider the contribution of each, as well as the solvent as a possible ligand – that is, *one must know the precise composition of one's nanoclusters in order to know all the possible alternative hypotheses* [81] *for the true stabilizer in the system.* However, the required precise composition information is almost never available – *and often not even considered* – in the literature. For example, the effects of an anion (often present from the decomposition of a metal salt) are frequently not considered when there is another potential, claimed stabilizer present. For instance, a common example is when a polymer or surfactant [82] is present and a metal halide precursor is reduced to form the $M(0)_n$ nanocluster, the effects of the halide are often completely ignored, while "polymer-"



[a] These are early examples of colloids, dating back to the time of Faraday [43].
[b] These colloids were first investigated by Hirai in 1979 [112a].
[c] These classic nanoclusters, characterized by TEM, ultracentrifugation, and EXAFS, are catalytically active for oxidative acetoxylation of ethylene with O_2 [85].
[d] Well-defined, catalytically active polyoxoanion-stabilized Ir(0) nanoclusters were first reportedin 1994 [14].
[e] These nanoclusters were first reported in 1981 [84].
[f] Nanoclusters of this type were recently reviewed [157]
[g] The structure of this massive carbonyl/nanocluster was recently established by single-crystal XRD; they are ligand-poisoned, however, and have not been shown to have catalytic activity [88].
[h] Classic carbonyl clusters, while compositionally well-defined and very stable, are typically not catalytically active until and unless some of the CO ligands are removed.

Scheme 5. Three modes of colloidal/nanocluster stabilization with selected examples.

or "surfactant-" stabilized nanoclusters are claimed. This phenomenon – *of interpreting one's data in terms of one's initial, assumed stabilizer hypothesis, without disproof of other, alternative hypotheses* – is widespread. It is *the* major conceptual and intellectual error in how nanocluster stabilization science is being done. Consequently, the conditions of each system, including the counterions of the precursor complexes, the solvent, the reaction atmosphere (O_2; leading to possible oxide formation), and so on must be taken into account when assigning the stabilizing entity in a nanocluster system. *In short, much of the existing nanocluster stabilization literature is primitive, unrefined, and based on a poor scientific method lacking disproof – caveat emptor*!

Indeed, a recent report from a collaborative effort of five prestigious groups active in nanocluster research acknowledges the myriad of stabilizers proposed in the literature, noting that in general it is not possible to "understand which (nanocluster) preparation method is the best among those proposed" [111]. The proliferation of claimed stabilizers in the literature can be traced to the only apparent requirement for claiming a novel stabilizers seems to be a TEM of the particles with an associated histogram, and occasionally an accompanying catalytic or other physical property test! The nanocluster/colloid literature has, consequently, grown at an alarming rate without any real idea of what the true, or best, stabilizer is.

Accordingly, in the following sections, the focus instead lies on the *mode* of stabilization with a few illustrative examples rather than attempting to review every stabilizer that has appeared in the literature – that is, this review does not portend to cover the recently noted "dizzying variety" [5] of nanocluster stabilizers that are employed in the literature. Representative examples of electrostatic/DLVO-type, steric, "solvent-only", and ionic liquid (IL) stabilization modes are covered in Table 1 and what follows. In Table 1 (in chronological order with respect to the first published report), the conditions under which the colloids or nanoclusters were prepared are listed, along with a brief commentary with respect to the key *compositional* information (or lack thereof) and other issues. In cases where more than one paper is referenced, the author (date) column applies to the first report, and the multiple references that follow note systems prepared under closely related conditions that have the same claimed stabilizer, compositional issues, and so on. A main finding from perusing Table 1 is that the *composition of nanoclusters needs to be rigorously established before any reliable discussion of how they are stabilized can ensue; a second important finding is that more in situ / operando measurements of nanoclusters (for example, the MW of the nanoclusters as measured by SAXS and/or analytical ultracentrifugation, as well as more XAFS and XANES studies) need to be undertaken.*

3.1. Electrostatic/DLVO-type stabilization

The classic theory of electrostatic colloidal stabilization was developed by Derjaugin, Landau, Verwey, and Overbeek, and is commonly referred to as DLVO theory [94]. DLVO theory predicts that nanocluster stabilization is based on a delicate balance in interparticle forces between repulsive Coulombic forces opposing attractive van der Waals forces. This theory was developed in the 1940s, is the most commonly used for, and seems to be the most accurate predictor of, the stability of so-called lyophobic colloids–colloids that are defined as having weak or no interactions between the colloid and the solvent [94] (the antithesis of lyophilic, putatively "solvent-only" stabilized colloids). Indeed, it was recently stated that "For colloid science the theory of DLVO stands at the same level of importance as does Darwin's theory of the origin of the species in Biology [95]" (with the understanding that the overall importance of DLVO theory is not being claimed to be at the same level as Darwin's theory of evolution!).

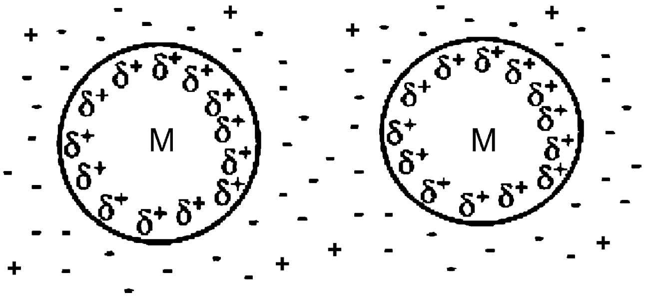


Fig. 1. Pictorial representation of two electrostatic/DLVO-type stabilized nanoclusters. The partial positive charge shown on the surface of the nanoclusters results from the electrostatic charge mirror generated from the attraction of anions to the coordinatively unsaturated, electrophilic nanocluster surfaces. Note that this cartoon, initially published elsewhere [9], has an exaggerated, non-charge-balanced emphasis on the anions to illustrate their importance. Reprinted with permission from Ref. [9]. Copyright 2002 American Chemical Society.

In DLVO-type electrostatic stabilization, the stabilizer of initial, if not primary, interest is the anion [78], as shown pictorially in Fig. 1. Anions, whether added to the solution separately or present from reduction of a metal salt precursor, will be bound to any previously coordinatively unsaturated, electrophilic nanocluster surface [27]. Hence, anions form a layer immediately adjacent to the nanocluster, providing the Columbic repulsion component of DLVO-type stabilization between two, now anionically charged particles, Fig. 1. Countercations are also present, to provide charge balance and complete the electronic multilayer. DLVO theory treats counterions as point charges, so small monoanions such as halides are among the closest "real-life", albeit still imperfect, examples of DLVO-type stabilization.

In the DLVO picture of colloidal stability, another important factor is the thickness of the Debye layer ($1/\kappa$). The Debye layer refers to the layer(s) of counterions surrounding the colloid, these ions being separated by solvent molecules. The thickness of the Debye layer affects the stability of the nanoclusters—generally, thicker Debye layers provide greater interparticle distances, reducing potentially agglomerative attractive van der Waals forces between the particles and increasing the nanocluster stability. The equation for the thickness (calculated in *m*; however, $1/\kappa$ values are typically on the order of nm) of the Debye layer, $1/\kappa$, is as follows (see equation 3.8.13a on p. 134 of reference [96];).

$$\frac{1}{\kappa} = \left(\frac{\varepsilon_0 \times \varepsilon_R \times k \times T}{\sum_i (z_i e)^2 \times c_{i_0}} \right)^{0.5}$$

Table 1

A compilation of selected literature examples, highlighting the need for compositional and *in situ* molecular weight information in many of the systems

Author (date)	System	Stabilizer compositions/related issues	Reference
Electrostatic/DLVO-*type* stabilization			
Turkevich, Stevenson, Hillier (1951)	An aqueous solution of $HAuCl_4$ was heated to boiling and reduced with an aqueous solution of citric acid	Potential surface contamination and/or contribution to stability from H_2O and Cl^-; citric acid can serve as both a reductant and a stabilizer; size distribution ranges from 100 to 500 Å; average composition and MW *unknown*	[83]
Schmid, Pfeil, Boese, Bandermann, Meyer, Calis, ver der Velden (1981)	$AuCl[P(C_6H_5)_3]$ was reduced with B_2H_6 in warm benzene; the dark precipitate is washed with CH_2Cl_2, and precipitated out with pentane	Characterized by TEM, HR-TEM, some STM, ^{31}P NMR, Mössbauer, and secondary ion MS; elemental analysis gives an average composition of $[Au_{9.2}(PPh_3)_2Cl]_n$, while sedimentation MW measurements give an average formula of $[Au_{\sim 55}(PPh_3)_{\sim 12}Cl_{\sim 6}]$; average composition and MW *known*	[84]
Vargaftik, Sargorodnikov, Stolarov, Moiseev, Likholobov, Kochubey, Chuvilin, Zaikosvsky, Zamaraev, Timofeeva (1985)	$Pd(OAc)_2$ was reduced with H_2 in acetic acid in the presence of either 1,10-phenanthroline (phen) or 2,2′-bipyridine (bipy)	Characterized by elemental analysis, TEM, SAXS, ^1H NMR, and EXAFS; workup under oxygen in acetic acid converts the original form of $[Pd_4phen(OAc)_2H_4]_n$ ($n \approx 100$) to the final colloidal composition of $[Pd_{\sim 561}phen_{\sim 60}(OAc)_{\sim 18}]$; average composition and MW *known*	[85]
Bönnemann, Brijoux, Brinkmann, Dinjus, Joußen, Korall (1991)	Halide salts of groups 6–11 metals are reduced with NR_4BEt_3H in THF	Halides present in 2–4 equiv. per equivalent metal; no halides reported in elemental analysis but other elements only add to 93.4%; proposed coordination of R_4N^+ surfactant is implausible; average; composition and MW *unknown*	[192]
Reetz, Helbig, Quaiser, Stimming, Breuer, Vogel (1995)	Pd colloids prepared electrochemically from Pd sheets in the presence of tetraalkylammonium salts in dried MeCN/THF	Br^- is present in 4% by elemental analysis; proposed coordination of R_4N^+ surfactant is implausible; average composition and MW *unknown*	[190]
Rothe, Pollmann, Franke, Hormes, Bönnemann, Brijoux, Sipen, Richter (1996)	$RhCl_3$ was the precursor for several colloids; reducing agent not stated; solvent not stated; at least two different surfactants added	XPS shows both residual halides and “sample contaminations” (C, O); XPS also shows “a large content of zerovalent Rh-atoms”, meaning the colloid is not in the fully reduced state; XANES also shows the presence of halides and incomplete reduction of the metal; average composition and MW *unknown*	[86]
Reetz, Winter, Breinbauer, Thurn-Albrecht, Vogel (2001)	Pd, Ni, and Pt/Pd colloids were prepared via electrochemical reduction of their corresponding metal sheet in the presence of surfactants in either THF or mixed THF:CH_3CN	Br^- present in surfactant; XRD shows some oxidation of the Pd colloids’ surfaces; using short-chain amine surfactants lead to the precipitation of the colloids; average composition and MW *unknown*	[195]
Steric stabilization			
Hirai, Chawanya, Toshima (1979)	Fe, Co, Ni, Cu, Ru, Rh, Pd, Pt, Au, Ag, Os, and Ir colloids were prepared by refluxing in an alcoholic solvent in the presence of PVP	Alcoholic solvent functions as a reducing agent and possibly also a stabilizer; precursors contain potential stabilizers such as Cl^- and H_2O; oxide surface layer likely after refluxing in air; average composition and MW *unknown*	[112a]
Terrill, Postlethwaite, Chen, Poon, Terzis, Chen, Hutchison, Clark, Wignall, Londono, Superfine, Falvo, Johnson, Samulski, Murray (1995)	An aqueous solution of $HAuCl_4 \cdot xH_2O$ was extracted into toluene with tetraoctyl-ammonium bromide, treated with an alkanethiol, and reduced with aqueous $NaBH_4$	Synthesis and nanocluster workup not performed in an inert atmosphere; potential surface contamination and/or contribution to stability from H_2O, Br^- and Cl^-; for two of the samples, elemental analysis of C, H, S, and Au adds to only ∼95%, ^1H NMR confirms the absence of free alkanethiol; IR spectra show characteristic stretches of alkane chains; average composition and MW *unknown*	[87]
Antonietti, Gröhn, Hartmann, Bronstein (1997)	$AuCl_3$ and $FeCl_3$ were reduced with N_2H_4 or $NaBH_4$ in aqueous solutions of polystyrene sulfonate microgels	Potential surface contamination and/or contribution to stability from H_2O and Cl^-; TEM shows extensive agglomeration, which the authors call “threads” or “nuggets”; no evidence that Au species are inside the microgels instead of on the sulfonate moieties; average composition and MW *unknown*	[151]
Zhao, Sun, Crooks (1998)	$CuSO_4$ was adsorbed into PAMAM dendrimers and reduced with $NaBH_4$ in water; later done with H_2PtCl_6 and H_2PdCl_6	HCl is added to adjust the pH; possible surface contamination and/or contributions to stability from H_2O and Cl^-; an oxide layer may be present due to synthesis under ambient conditions but was not investigated; average composition and MW *unknown*	[132,133,135,137,139]
Balogh, Tomalia (1998)	$Cu(OAc)_2$ was adsorbed into PAMAM dendrimers and reduced with N_2H_4 in aqueous solution	Potential surface contamination and/or contribution to stability from H_2O and OAc^-; Cu colloids were easily oxidized upon exposure to atmospheric oxygen; no TEM or elemental analysis done; average composition and MW *unknown*	[140]

Table 1 (*Continued*)

Author (date)	System	Stabilizer compositions/related issues	Reference
Whilton, Berton, Bronstein, Hentze, Antonietti (1999)	$(H_3N)_4Pt(NO_3)_2$, $PdCl_2$, $(py)_4RhCl_3$, or Na_2PtCl_6 were reduced with $NaBH_4$ in water or NaOH in solutions of polystyrene sulfonate microgels, then incorporated into a porous silica template	Potential surface contamination and/or contribution to stability from H_2O, OH^- and Cl^-; B incorporation possible; exposure to gaseous HCl during silica templating; potentially stabilizing MeOH produced by templating reaction; final nanocluster in template are heated under O_2 for 12 h; average composition and MW *unknown*	[152]
Zhao, Crooks (1999)	$Cu(NO_3)_2{\cdot}2.5H_2O$ was adsorbed into OH-terminated PAMAM dendrimers, the pH was adjusted with NaOH, and then reduced with $NaBH_4$; Cu was later displaced with aqueous solutions of $AgNO_3$, $HAuCl_4$, K_2PdCl_4, or K_2PtCl_4	Potential surface contamination and/or contribution to stability from H_2O, OH^-, Cl^-, $NO_3{}^-$; B incorporation possible; no proof that colloids are stabilized only by the dendrimer; average composition and MW *unknown*	[134]
Stavens, Pusztay, Zou, Andres, Wei (1999)	Au colloids were generated as aerosols and bubbled into mesitylene solutions of resorcinarenes	TEM shows wide size distribution (3–15 nm); colloids precipitate upon removing excess resorcinarene or changing solvents; resorcinarenes are exchanged by added thiols; average composition and MW *unknown*	[167]
Bronstein, Chernyshov, Valetsky, Wilder, Spontak (2000)	$H_2PtCl_6{\cdot}6H_2O$, K_2PtCl_4, $AuCl_3$, or Na_2PdCl_4 were reduced with $NaBH_4$ in either a water/acetone or water/ethanol solution in the presence of PODS	Potential surface contamination and/or contribution to stability from H_2O, OH^-, and/or Cl^-; B incorporation possible; colloids not prepared under an inert atmosphere; possible reduction by ethanol and then contribution to stabilization by the resulting alkoxide; possible contribution to stability from silanol moieties; average composition and MW *unknown*	[128]
Tran, Powell, Dahl (2000)	$[Pd(PEt_3)_2Cl_2]$ and $[Au(PPh_3)Cl]$ were stirred under CO for 2 days in a DMF solution containing NaOH pellets, filtered into $[PPh_4]Br$; the dark brown solid was extracted with MeOH, MeCN, and THF	Characterized with single-crystal XRD data with crystals from two separate preparation; no catalytic tests performed (not expected to be catalytic due to strong ligation of ∼74% of the surface atoms by CO and PEt_3); elemental analysis would compliment the XRD data *precise composition known to be* $Pd_{145}(CO)_{\sim 60}(PEt_3)_{30}$*; average MW known*	[88]
Wang, Yang, Zheng, Carducci, Jiao, Seraphin (2001)	$HAuCl_4$ was reduced with an aqueous solution of $NaBH_4$ in the presence of $(n\text{-}C_8H_{17})_4NBr$ and various generations of dendrons	Potential surface contamination and/or contribution to stability from H_2O, Br^-, Cl^-; B incorporation possible; notes that a “significant amount of black precipitate” is generated if the reduction is carried out in the absence of $(n\text{-}C_8H_{17})_4NBr$, indicating a contribution to stability from the surfactant; TEM shows agglomeration; reaction presumably carried out without air-free techniques; average composition and MW *unknown*	[142]
Pusztay, Wei, Stavens, Andres (2001)	Au colloids were generated as aerosols and bubbled into mesitylene solutions of resorcinarenes; the resorcinarenes were then crosslinked	Colloids precipitated within hours; TEM showed “clumps rather than isolated particles”; the authors suggest catalytic ability but never test it; average composition and MW *unknown*	[145]
Cordente, Respaud, Senocq, Casanove, Amiens, Chaudret (2001)	$Ni(COD)_2$ was reduced with 3 bar H_2 in THF in the presence of hexadecylamine or trioctylphosphine oxide	No elemental analysis done; TEM shows agglomerated colloids; no controls done with the Ni precursor alone on the TEM grid to check for nanocluster formation under the TEM beam; average composition and MW *unknown*	[172]
Li, El-Sayed (2001)	$PdCl_2$ or K_2PdCl_4 were reduced by $NaBH_4$ or ethanol in aqueous solutions of either PAMAM dendrimers, PVP, or poly(styrene)-*block*-poly(sodium acrylate)	Potential surface contamination and/or contribution to stability from H_2O, OH^-, Cl^-; B incorporation possible; PAMAM solution acidified with HCl before reduction; PVP and block copolymer solutions were refluxed under air; some precipitation of the colloids is noted after catalysis; average composition and MW *unknown*	[115]
Floriano, NobleIV, Schoonmaker, Poliakoff, McCarley (2001)	$Cu(NO_3)_2{\cdot}2.5H_2O$ in methanolic solution was adsorbed into amine-terminated PPI dendrimers with diaminobutane cores and reduced with $NaBH_4$	Potential surface contamination and/or contribution to stability from H_2O, OH^-, MeO^-; $NO_3{}^-$; B incorporation possible; TEM shows agglomeration; average composition and MW *unknown*	[143]
Kim, Tripp, Wei (2001)	Au colloids stabilized by citrate were treated with a solution of resorcinarenes in THF	Both citrate and the resorcinarene could serve as the stabilizer; possible surface contamination by H_2O; TEM shows near-monodisperse 70 ± 5 nm nanoclusters; average composition and MW *unknown*	[163,164]
Bucher, Hormes, Modrow, Brinkmann, Waldöfner, Bönnemann, Beuermann, Krischok, Maus-Friedrichs, Kempter (2002)	Pd colloids were prepared by reducing $PdCl_2$ with NR_4BEt_3H in THF	Elemental analysis shows between 1.4 and 8.1 Cl atoms per Pd (3.1–13.2 Cl per *surface* Pd) and also the presence of the surfactant; XANES, and metastable impact electron spectroscopy (MIES) suggest “that the chlorine is present on the inside of the protection shell, located between palladium core and $N(alkyl)_4$ groups” *anionic stabilization by halides with a contribution by the countercation is recognized; composition partially determined but average MW unknown*	[193,194]

Niu, Crooks (2003)	$CuCl_2 \cdot H_2O$ or $Pd(OAc)_2$ was adsorbed into hexanoyl- or palmitoyl-modified PPI dendrimers in $CHCl_3$/MeOH and reduced with $NaBH_4$	Potential surface contamination and/or contribution to stability from H_2O, Cl^-, OH^- and OAc^-; B incorporation possible; nanocluster solution changes color in the presence of atmospheric O_2; average composition and MW *unknown*	[138]
Biffis, Orlandi, Corain (2003)	$Pd(OAc)_2$ or $PtCl_2(CH_3)CN$ was reduced with either EtOH or $NaHBEt_3$ in the presence of either amine- or pyridine-terminated microgels in CH_2Cl_2 or CH_3CN	Potential surface contamination and/or contribution to stability from H_2O, CH_3CN, OH^- and OAc^-; B incorporation possible; average composition and MW *unknown*	[154,155]
Chauhan, Rathore, Chauhan, Krawicz (2003)	Reduction of $Pd(OAc)_2$ with PMHS in a benzene/acetic acid solvent; separately done with Ag(OAc)	PMHS can serve as reductant and stabilizer; potential contribution to stability by acetate; TEM shows extensive agglomeration; average composition and MW *unknown*	[120,129,130]
Ramirez, Jansat, Philippot, Lecante, Comez, Masdeu-Bultó, Chaudret (2004)	Pd_2(dibenzylidene acetone)$_3$ or $[Pd(C_3H_5)Cl]_2$ were reduced with 3 bar H_2 in the presence of hexadecylamine, bis-(diphenylphosphino) decane or bis-(diphenylphosphinoethyl)-phenylphosphine in THF or toluene	Potential surface contamination and/or contribution to stability from Cl; TEM shows extensive agglomeration; using THF led to increased stability (as measured by TEM), indicating a contribution to stability from the solvent; average composition and MW *unknown*	[164]
Narayanan, El-Sayed (2004)	K_2PdCl_4 was reduced with $NaBH_4$ in aqueous solutions of either PVP or PAMAM dendrimers	Potential surface contamination and/or contribution to stability by H_2O, B, and Cl; size distribution monitored by TEM but the presence of bulk metal in the reaction flask means TEM analysis is not representative of the whole sample; average composition and MW *unknown*	[113]
Patakfalvi, Virányi, Dékány (2004)	$AgNO_3$ was reduced with hydroquinone or sodium citrate in the presence of PVP or PVA in water	Both PVA and citrate can serve as the reducing agent and the stabilizer; potential surface contamination by H_2O; an oxide layer may be present due to synthesis under ambient conditions; average composition and MW *unknown*	[124]
Pelzer, Laleu, Lefebvre, Philippot, Chaudret, Candy, Basset (2004)	$RuCl_3 \cdot 3H_2O$ was used to prepare Ru(COD)(COT), which was reduced with 3 bar H_2 at 193 K in the presence of $H_3SiC_8H_{17}$	Elemental analysis results indicate that “about 0.55 silicon atoms per ruthenium atoms are grafted on the metal surface and about 0.7 octyl chains remain bonded per silicon atom”; TEM shows agglomeration; Ir and ^1H, ^{13}C, and ^{29}Si NMR indicate that organosilane fragments are bonded to the nanocluster surfaces; average composition of surface Ru atoms of $Ru_s[Si(n\text{-}C_8H_{17})_{0.7}]_{1.2}$ is proposed for the $Ru_{\sim586}$ clusters; average total composition not proposed; average MW *not known*	[89]
Electrosteric stabilization			
Lin, Finke (1994)	$(Bu_4N)_5Na_3[(1,5\text{-COD})Ir \cdot P_2W_{15}Nb_3O_{62}]$ was reduced with H_2 in acetone solvent under strict exclusion of O_2 and H_2O	Balanced (average) reaction stoichiometry obtained en route to providing nanocluster composition and stabilization mode; elemental analysis and ultracentrifugation MW measurements determine the average composition of $[Ir(0)_{\sim300}(P_4W_{30}Nb_6O_{123}{}^{16-})_{\sim33}](Bu_4N)_{\sim300}Na_{\sim233}$; average composition and MW *known*	[6,9,10,11,12,14,78,79,90,178]
Aiken III, Finke (1999)	$(Bu_4N)_5Na_3[(1,5\text{-COD})Rh \cdot P_2W_{15}Nb_3O_{62}]$ was reduced with H_2 in acetone solvent under strict exclusion of O_2 and H_2O	Ion-exchange resin studies demand that the polyoxoanion is the stabilizing entity; elemental analysis and EDS establishes the average composition as $[Rh(0)_{\sim7}(P_4W_{30}Nb_6O_{123})(Bu_4N)_{\sim5.5}Na_{\sim10.5}]_{\sim340}$; average composition *known, but not MW*	[15,50,149]
Putative “Solvent-only” Stabilization			
Klabunde, Efner, Murdock, Ropple (1976)	Ni·solvent (hexane, toluene, or THF) slurries were prepared by co-condensation of vaporized Ni atoms and the solvent	SEM shows agglomeration and μm sized particles; solvent:metal ratio determined by desorption of organics upon pyrolysis, but no elemental analysis was done; average composition and MW *unknown*	[35]
Cardenas-Trivino, Klabunde, Dale (1987)	Pd atoms were prepared by metal atom vaporization, followed by condensation with a non-aqueous solvent to form Pd colloids	Size dispersion not given; TEM shows aggregation; electrophoresis proves charge is scavenged from the reaction environment; average composition and MW *unknown*	[204]
Bönneman, Korall (1992)	$TiCl_4$ in THF was reduced with $K[BEt_3H]$ to form “Ti·0.5 THF”	Elemental analysis shows the presence of B, K and Cl; XRD analysis shows the presence of KCl; XPS data indicate that the colloids formed are “almost as reduced as titanium metal”; oxides (TiO_x) seem likely; average composition and MW *unknown*	[86,198a]
Reetz, Lohmer (1996)	Decomposition of Pd electrode or thermal decomposition of $Pd(OAc)_2$, both in propylene carbonate	In the electrode preparation, both Cl^- and ethanol are present as potential stabilizers; in the thermal decomposition preparation, OAc^- is a potential stabilizer: TEM on both systems shows wide size distributions and marked aggregation; average composition and MW *unknown*	[39]

Table 1 (*Continued*)

Author (date)	System	Stabilizer compositions/related issues	Reference
Franke, Rothe, Pollmann, Hormes, Bönnemann, Brijoux, Hindenburg (1996)	$TiBr_4 \cdot 2THF$ was reduced with $K[BEt_3H]$ in THF	Elemental analysis shows 5.5% K and 0.7% Br; no B analysis reported; XPS shows evidence of surface oxidation; most observations interpreted in terms of Ti-THF coordination (Ti 2p BE shift in XPS, energy shift in XANES analysis, etc) could also be attributed to surface oxidation; also applied to colloids of Zr, V, Nb, and Mn; average composition and MW *unknown*	[198b]
Dhas, Cohen, Gedanken (1997)	Pd_2(dibenzylidene-acetonate)$_3$ in mesitylene was subjected to ultrasound irradiation under Ar	Elemental analysis shows >41% carbon and <1.5% hydrogen; authors claim a "carbon-activated palladium powder"; no powder XRD peaks until heating to 300–400 °C; XPS C 1s spectrum is consistent with graphitic carbon; average composition and MW *unknown*	[91]
Vidoni, Philippot, Amiens, Chaudret, Balmes, Malm, Bovin, Senocq, Casanove (1999)	Ru(1,5-COD)(COT) was reduced with 3 bar H_2 in various ratios of MeOH:THF	Possible methoxide stabilizer; passivating oxide layer present by XRD and XPS; TEM shows aggregation of particles; particles isolated by precipitation cannot be redissolved; average composition and MW *unknown*	[199]
Collier, Iggo, Whyman (1999)	Pd and Pt atoms were prepared by metal atom vaporization followed by condensation with organic solvents; in some cases, proprietary stabilizing agents "KD1" and "KD2" were used	No TEM shown; histograms from TEM data show bimodal size distribution; TEM is noted to look like "frogspawn" or "raspberries," indicating aggregation; not "solvent-only" stabilized given the added stabilizing agents (also, no evidence that KD1 and KD2 are superior stabilizing agents – or even information on what they are!); average composition and MW *unknown*	[200]
Wang, Ren, Den, Gui, Tang (2000)	$H_2PtCl_6 \cdot 6H_20$ was heated in a 0.5 M NaOH solution in ethylene glycol; aqueous solutions of either $RhCl_3 \cdot 3H_2O$ or $RuCl_3 \cdot 6H_2O$ were heated in a 0.5 M NaOH solution in water	Possible surface contamination and/or contribution to stability by OH^-, Cl^-, and H_2O; preparations at pH <12 form bulk metal instead of colloids; TEM shows agglomeration; XPS and elemental analysis measurements were taken only after repeated washings in HCl and acetone; average composition and MW *unknown*	[201]
Pelzer, Vidoni, Philippot, Chaudret, Collière (2003)	$RuCl_3 \cdot 3H_2O$ was used to prepare Ru(1,5-COD)(COT), which was reduced with 3 bar H_2 in either a pure alcohol or an alcohol/THF mixture	Possible surface contamination and/or contribution to stability by alcohols; alcoholic solvents can serve as the reductant and the stabilizer; THF may coordinate to the nanocluster surface; no elemental analysis performed; TEM shows agglomeration; average composition and MW *unknown*	[203]
Pelzer, Philippot, Chaudret (2003)	$RuCl_3 \cdot 3H_2O$ was used to prepare Ru(1,5-COD)(COT), which was reduced with 3 bar H_2 in heptanol	Alcoholic solvents can serve as the reductant and the stabilizer; ^1H and ^{13}C NMR indicate coordination of heptoxy molecules on the nanocluster surface; TEM shows some agglomeration; elemental analysis "indicate[s] the presence of ca. 70% Ru and ca. 1 heptanol: 7.5 Ru"; *estimated composition proposed; no MW information*; additional evidence desirable for this interesting system	[92]
Ionic liquid (IL) stabilization			
Dupont, Fonseca, Umpierre, Fichtner, Teixeira (2002)	$[(1,5\text{-COD})IrCl]_2$ or $[(1,5\text{-COD})Ir(py)(PCy_3)]\text{-}[PF_6]$ was reduced under 4 atm H_2 at 75 °C in [bmim][PF_6]	Cl^- present; TEM shows extensive agglomeration; IL not predicted to stabilize by DLVO theory or through steric stabilization – i.e., unknown stabilization mechanism; average composition and MW *unknown*	[216]
Scheeren, Machado, Dupont, Fichtner, Texeira (2003)	Pt_2(bis-dibenzylidene acetone) was reduced with 4 atm H_2 in [bmim][PF_6]	Cl^- present in IL in ∼1.4 mg/L levels as synthetic impurity; TEM shows extensive agglomeration; EDS was not able to determine the constituent elements of the colloids in IL; average composition and MW *unknown*	[219]
Itoh, Naka, Chujo (2004)	$HAuCl_4$ was reduced with $NaBH_4$ in the presence of an imidazolium-based dichloride IL	Cl^- present from precursor and IL; all colloids are in an aqueous solution with IL present; TEM shows a wide size distribution (no size distribution given); particles agglomerated with anion exchange; average composition and MW *unknown*	[220]
Cassol, Umpierre, Machado, Wolke, Dupont (2005)	Chloropalladated propargyl amine was reacted with a large excess of dimethylallene in CH_2Cl_2	One equiv. Cl^- present per equiv Pd; TEM shows agglomeration; no elemental analysis done; average composition and MW *unknown*	[221]
Ott, Cline, Deetlefs, Seddon, Finke	$[(1,5\text{-COD})Ir(CH_3CN)_2][BF_4]$ was reduced in acetone with varying equivalents of imidazolium-based ILs	Increased solution stability observed with increasing equivalents of IL; ^2H NMR evidence of *N*-heterocyclic carbene formation from the imidazolium cation; carbene implicated as stabilizer; average composition and MW *unknown*, but nature of stabilizer from ILs elucidated	[241]
Ott, Campbell, Seddon, Finke, (2006)	$[(1,5\text{-COD})IrCl]_2$ was reduced with H_2 in acetone, neat IL, or acetone plus 0–5 equiv.	1 equiv.; IL poisons previously active nanocluster catalysts in acetone; average composition and MW *unknown*, but nature of poison from ILs implicated	[93]

Above, ε_0 is the permittivity of free space, ε_R the dielectric constant of the medium (the solvent), k the Boltzmann constant, T the temperature, z_i the ion valency, e the charge on an electron, and c_{i0} is the concentration of the ion species, i, in the bulk solution [96]. Of note with regard to the Debye layer is the prediction that a thicker diffuse layer – and consequently better stabilization – will be achieved in the presence of *high dielectric constant* solvents. This DLVO theory prediction has been investigated elsewhere [97] using solvents of varying ε. It was found that the DLVO theory prediction generally follows even for the case of the traditionally weakly coordinating anion BF_4^-, with polar, high ε solvents like *N*-methylacetamide ($\varepsilon = 165$) and propylene carbonate ($\varepsilon = 69$) [39] providing considerably more stable nanoclusters than lower ε solvents such as acetone ($\varepsilon = 20$) [97].

An important, almost never cited fact from one of Turkevich's classic papers on Au colloids merits mention here. In that 1985 study, Turkevich used combined electrophoresis plus ultracentrifugation to show that a single negative charge was present in a Au colloid of ca. 23–27 Å on a side [29b]. The important implications here are two-fold: (i) that small amounts of charge provide DLVO-type electrostatic stabilization, and (ii) studies analogous to these Turkevich did, but on modern transition-metal nanoclusters, to determine their charge per surface volume are badly needed.

Care must be taken to apply DLVO theory only to appropriate nanocluster systems [95,98]. DLVO theory was not designed to account for counterions with multiple charge or sterically stabilized systems. Additionally, DLVO theory does not appear to work well in more concentrated systems ($>5 \times 10^{-2}$ M), where dispersion forces (induced dipole-induced dipole interactions) may dominate electrostatic forces [98]. It is also not possible to find "real-life" examples of ideal, exactly DLVO-type *point charge* electrostatic stabilization since no such ions actually exist. Perhaps for these reasons, DLVO theory continues to be widely discussed and somewhat controversial [99–101], including, for example, the addition of so-called "extra-DLVO" forces [98] (including hydrogen bonding and the hydrophobic effect, hydration pressure, non charge-transfer Lewis acid/base interactions, and steric interactions [101]). In spite of the limitations discussed above, DLVO theory (i) is the first place one should turn in thinking about electrostatic colloidal/nanocluster stability, and (ii) does correctly predict that discussions of nanocluster stability should start with coordinating *anions plus high dielectric constant solvents* [97,105].

3.2. Steric stabilization

As mentioned earlier, one mode of nanocluster one non-DLVO theory mode of stabilization. In some sterically stabilized systems, the surfaces of the nanoclusters may be ligated (e.g., in one limit by strong ligands such as thiols [102] or carbonyls [103]). Very small ligand-stabilized (carbonyl) clusters, such as $Ir_4(CO)_{12}$, can be considered ligand-stabilized as well as ligand-*poisoned* clusters—that is, they possess coordinatively saturated, 18 electron metal centers and are not catalytically active. However, larger nanoclusters or colloids with surface bound ligands may still be catalytically active provided some fraction of the surface sites remain coordinatively unsaturated.

3.2.1. Polymers

One of the most frequently studied types of steric stabilization is stabilization by polymers. Polymers stabilize at least in part by ligation of nanocluster surface atoms, but also by physically occupying space around the nanoclusters, thereby sterically discouraging direct contact between the nanoclusters. *However, there is little direct evidence for the latter mode of polymer stabilization.* Nanoclusters of many transition metals (including Au, Ag, Pd, Pt, and Ir, among others) have been prepared with a variety of polymeric additives, the two most frequently employed polymers being poly(vinylpyrrolidone) and poly(vinyl alcohol) (*vide infra*). A survey of the literature indicates that above a "critical" amount of polymer, the stabilization is independent of the quantity of polymer used; however, it has been shown that the polymer chain *length* does have some influence on the stability of Ni colloids [104]. Worth noting is that many polymers contain adventitious water [105], leading to compositionally ill-defined nanoclusters that may contain surface H_2O, OH^-, or O^{2-} ligands. Studies elsewhere show that the amount of H_2O present during nanocluster formation influences both the formation and stabilization of prototype $Ir(0)_n$ nanoclusters [105,106], but also that this water can be effectively removed by drying polymer solutions over activated molecular sieves for ≥12 h [105]. In addition, metal halide nanocluster precursors are often used, raising the issue of a coordinated halide, DLVO-type contribution to stability rather than the assumed polymeric (steric) stabilization. A drawback of polymer-stabilized nanoclusters is that polymeric coordination (e.g., with the strongly coordinating polymer poly(vinylpyridine) [107–110]) or steric blocking of the surface atoms often compromises the catalytic activity.

Another little studied or even cited issue is that polymer stabilization is typically written as if one polymer chain stabilizes one nanocluster. In fact, *one would expect longer polymers to attach to more than one nanocluster*, and Taylor dispersion measurements (of the hydrodynamic radius of the nanoclusters in solution) indicate that one polymer chain can in fact attach to multiple nanoclusters [111], as illustrated pictorially in Fig. 2 below. The nanocluster science community would be well served if Taylor dispersion measurements on nanoclusters [111] were much more common.

The most commonly used polymeric nanocluster stabilizer is poly(vinyl pyrrolidone) (PVP). There is an extensive literature documenting the use of PVP as a nanocluster stabilizer [112], including a classic study of colloids of several metals stabilized with PVP by Hirai et al. in 1979 [112a]. PVP-stabilized nanoclusters have been shown to be active in several catalytic reactions, including hydrogenation [107,112a,113], the Suzuki reaction [114,115], and the Heck reaction [116]. However, these PVP-protected nanoclusters are frequently prepared in water beginning with chlorinated precursors (such as $RhCl_3 \cdot H_2O$ [112a] and $HAuCl_4$ [117]), leading, once again, to the possibility of halide stabilization and compositionally ill-defined colloidal surfaces. Additionally, as in prototype PVP-stabilized nanoclusters [112a], an alcohol is frequently used as both sol-

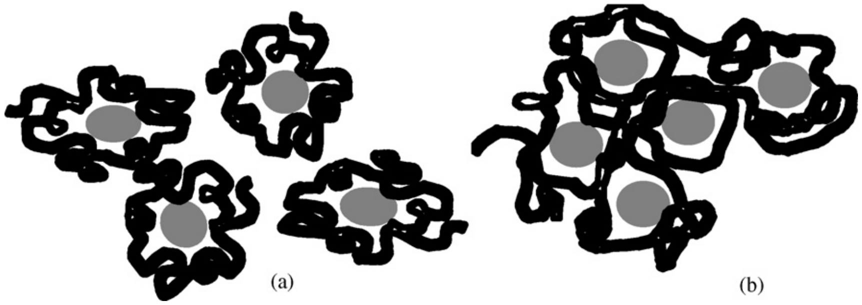


Fig. 2. A cartoon of two possible polymeric stabilization modes. (a) Shows stabilization of nanoclusters with individual polymer chains as often assumed in the literature, while (b) shows stabilization of multiple nanoclusters by a single polymer chain as supported by Taylor dispersion measurements [111].

vent and reducing agent. Again, this leads to compositionally ill-defined colloid surfaces which may be coordinated by alkoxy molecules or possibly the resultant oxidized carbonyl product or its oligomers (e.g., H_2CO from CH_3OH or oligomers of H_2CO).

The 5 criteria method outlined earlier has been employed to test PVP for its ability to stabilize $Ir(0)_n$ nanoclusters [106]. PVP was tested as a steric stabilizer (but in the presence of BF_4^- from the decomposition of the organometallic precursor $[(1,5\text{-COD})Ir(CH_3CN)_2][BF_4]$), and in comparison to the $P_2W_{15}Nb_3O_{62}{}^{9-}$ polyoxoanion (electrostatic) stabilizer (Fig. 2, *vide supra*). Additionally, four other polymeric nanocluster stabilizers reported previously were investigated with the 5 criteria method, specifically poly(methyl methacrylate) (PMMA) [118], poly(styrene) (PS) [119], poly(methylhydrosiloxane) (PMHS) [120], and poly(bis(ethoxy)phosphazene) (PBEP) [121], all of which have been implied in the literature to be excellent nanocluster stabilizers [118–121]. The main findings from the five criteria study [105] are that: (i) using dried polymers is important for preparing transition-metal nanoclusters in (dry) organic solvents; (ii) 1 equiv. of BF_4^- plus the high dielectric constant solvent propylene carbonate provides at least as much nanocluster formation and stabilization ability as does 1 monomer-equiv. of dried PVP (by monomer-equivalents we are indicating the usual situation [112] in which the number of equivalents of monomer units added is calculated using the monomer's MW [105,112]); (iii) adding 40 monomer-equiv. of dried PVP plus having 1 equiv. BF_4^- present is necessary to achieve isolable and redissolvable $Ir(0)_n$ nanoclusters; (iv) 40 monomer-equiv. dried MW_{ave} = 10,000 g/mol PVP plus 1 equiv. BF_4^- is inferior for *both* nanocluster *formation and stabilization* when compared to then current "Gold Standard" (poly)anion of 1 equiv. $P_2W_{15}Nb_3O_{62}{}^{9-}$, at least for $Ir(0)_n$ nanoclusters and under the conditions of 22 °C and 40 psig H_2 in propylene carbonate; (v) 40 monomer-equiv. of dried PVP added to nanoclusters stabilized by 1 equiv. $P_2W_{15}Nb_3O_{62}{}^{9-}$ *slows* the catalytic activity and total catalytic lifetime by ca. 50%; and (vi) of the four other polymers, PMMA was the most similar to PVP in providing a modest level of stabilization as measured by the five criteria—PS, PMHS, and PBEP were all found to be ineffective for the formation and stabilization of catalytically active $Ir(0)_n$ nanoclusters.

Separately, poly(vinyl alcohol) (PVA) has also been studied as a steric stabilizer, beginning with the work of Rampino and Nord in 1941 on Pd and Pt colloids [122,123]. Since then, PVA has been used to stabilize nanoclusters of many different metals, including for example Ag [124,125] and Au [126]. Grätzel studied PVA-stabilized Pt colloids for their efficacy in oxidizing methyl viologen during the light-induced H_2 evolution from water as part of photo redox processes for solar cells [127]. PVA polymers in nanocluster systems have the potential to serve as both the reductant of the organometallic complex *and* the nanocluster stabilizer. Again, compositionally poorly defined nanoclusters are the rule to date in putative "PVA-stabilized" nanoclusters, so that more study is needed to have any true idea of how PVA really ranks as a nanocluster stabilizer.

3.2.2. Siloxane polymers

Recently, siloxane polymers (such as poly(octadecylsiloxane) (PODS) or poly(methylhydrosiloxane) (PMHS as above)) have been used to stabilize transition-metal nanoclusters [120,128–130]. In the first report of siloxane stabilized nanoclusters, PODS was used to stabilize Au, Pd, and Pt nanoclusters [128]. The silanol moieties on the partially condensed siloxane polymer were capable of reducing the Pd and Pt precursors, offering the advantage of simple reaction conditions. Although the condensed polymer is expected to provide some steric stabilization, TEM micrographs show *extensively agglomerated nanoclusters*. Additionally, the presence of H_2O, Cl^-, and in some cases EtOH complicates assignment of the true stabilizer and leads to compositionally ill-defined clusters [128]. In a series of other papers [120,129,130], PMHS was used to generate and stabilize Pd and Ag nanoclusters. The authors claimed that reduction of the organometallic precursor by the Si–H bonds present simplifies the reaction conditions; however, this possible advantage is overshadowed by the ill-characterized nature of the oxidized product/stabilizer as well as by the extensive nanocluster agglomeration shown by TEM [120]. Additionally, after the nanoclusters were isolated from the solution, SEM showed that the average size of the nanoclusters had grown six- to eight-fold from 6 ± 1 nm in solution to 40–50 nm in the solid state. Given the above evidence, it appears that siloxane polymers are not superior steric stabilizers for transition-metal nanoclusters as claimed by others [120,129,130]. At the minimum, siloxane polymers are untested stabilizers, versus the alternative hypothesis that other common stabilizers are actually superior.

3.2.3. Dendrimers

Dendrimers have also been recently explored as structurally well-defined steric stabilizers. Most dendrimers employed for nanocluster synthesis and stabilization are nitrogen-based, such as poly(amidoamine) (PAMAM) and poly(propylene imine) (PPI) [131]. Dendrimers have been well-studied as nanocluster stabilizers, beginning with the pioneering work of Crooks and his co-workers. Crooks first reported the preparation of Cu nanoclusters in PAMAM dendrimers [132] in 1998, and this work has been expanded upon by his group [133–140] and others [141–144]. Dendrimers have a precisely branched, well controlled structure (with correspondingly difficult syntheses). It has been demonstrated by spectrophotometric titration [132] that the number of metal atoms adsorbed into the dendrimer interior corresponds to the number of interior tertiary amines. Adsorption of the metal ion on the *surface* amine groups of the dendrimer is usually undesirable, as the nanoclusters then form on the exterior of the dendrimer are susceptible to aggregation via intermolecular collisions. Adjusting the pH of the dendrimer solution with HCl is a common method for protonating the exterior amine groups and assuring the organometallic precursor is selectively adsorbed in the interior of the dendrimer [137]. Using dendrimers has the advantage of good size control of the nanoclusters by selecting the dendrimer with the precise number of interior tertiary amines (=desired number of nanocluster precursor atoms). Hence, the metal atoms are in the interior of the dendrimer before reduction and the newly formed nanocluster has a dendritic stabilizer already in place [131], as in Fig. 3. Dendrimers have, therefore, some very nice architectural features useful in preparing nanoclusters.

However, there are also limitations when using dendrimers as steric stabilizers. The major drawback of at least early dendrimers is their limited solubility. Dendrimers such as the most commonly used PAMAM dendrimer are typically soluble in only a few solvents (such as water, alcohols, and weak acids, and usually only as a 1% solution after tumbling for 24 h [145]), which greatly limits their utility. Through the functionalization of the terminal groups of PAMAM, it is now possible to prepare dendrimer-encapsulated nanoclusters in organic solvents [140]. Although the method of preparation leading to intra-dendrimer nanoclusters has been shown to lead to stable nanoclusters [132–144] (including bimetallic nanoclusters [146,147]), their utility as catalysts may be diminished due to low substrate access caused by a dense layer of terminal groups in high generation dendrimers [148]. Additionally, the CS_2 poisoning method [149] to titrate the number of catalytically active sites has not been performed, but needs to be, for dendrimer-stabilized nanoclusters. A limited permeability of the dendrimer surface (and hence access for catalytic substrates) has been demonstrated by showing that thiols can extract Pd nanoclusters from the interior of PAMAM dendrimers [150]. Overall, the useful architectural features of dendrimers seem well established, but their utility as nanocluster stabilizers is diminished by their extremely limited solubility in common organic solvents [145] and their unranked, sterically hindered, level of catalytic activity.

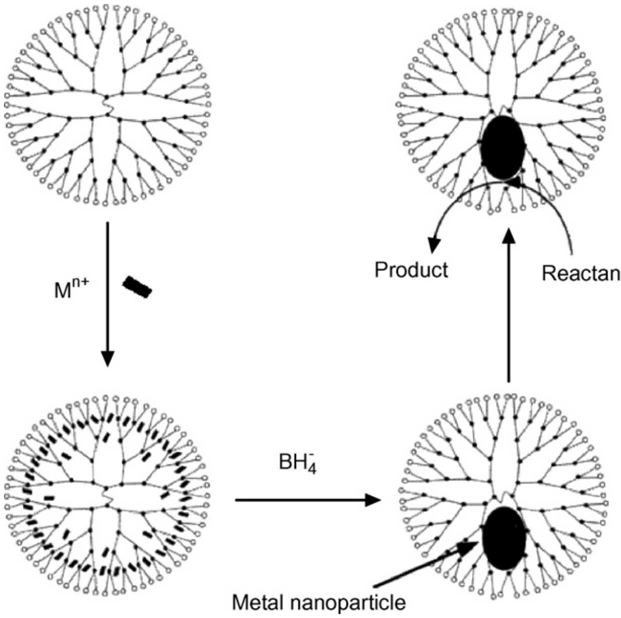


Fig. 3. Formation of dendrimer-encapsulated nanoparticles. The bar adjacent to the first arrow is another indication of a M^{n+} in the dendrimer. Reprinted with permission from Ref. [131]. Copyright 2001 American Chemical Society.

3.2.4. Microgels

Transition-metal nanoclusters have also been suspended in sterically stabilizing microgels [151–155]. These cross-linked globular macromolecules have been shown to be competent nanocluster stabilizers, yielding in one case Pd nanoclusters of 2.3 ± 0.8 nm which serve as catalysts (or possibly catalyst precursors [156]) for the Suzuki reaction [154]. Similar Pd nanoclusters suspended in functionalized microgels were shown to be catalytically active for the Heck reaction of activated aryl bromides [155]. However, microgels have a less precisely controlled structure than dendrimers, offering reduced control over the size and, presumably, also the desired properties of the nanoclusters. Hence, microgels do not appear to be preferred stabilizers for modern transition-metal nanoclusters where determining the composition of the resultant nanocluster is one key to understanding their stability.

3.2.5. Alkanethiol (and other) surfactants

Of the surfactant stabilizers employed in the literature, alkanethiols are perhaps the most frequently employed (as recently discussed by Murray and his co-workers [157]). Due to strong bonding between the RS^- group and the electrophilic nanocluster surface, alkanethiols become covalently linked to the nanocluster surface, making these *ligand* stabilized nanoclusters [157]. This coordination decreases the number of surface atoms available for catalysis. Thiol-stabilized Ag nanoclusters recently have been prepared using supercritical CO_2 as solvent; however, these nanoclusters had a wide size distribution of ±92% [158]. It is not known if oxidation and RS–SR coordination to the surface of the nanocluster occurs as has been postulated for RS^-/Au self-assembled monolayers [159]. Additionally, catalytic conversion of thiols to disulfides has recently been reported for Ru nanoclusters [160]. Although some surfactant stabilized nanoclusters are

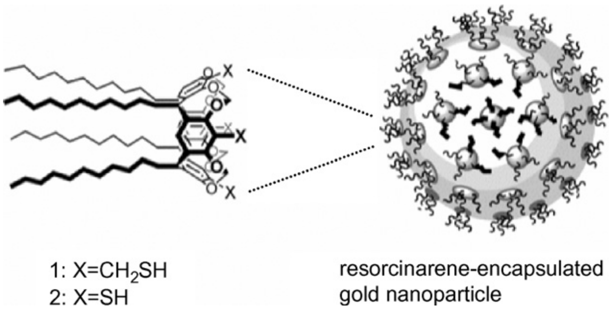


Fig. 4. An example of a tetrathiolated resorcinarene, and a cartoon for their ligation of an Au nanoparticle. Reprinted with permission from Ref. [168]. Copyright 2002 American Chemical Society.

catalytically active [161], surfactants are generally not preferred stabilizers for nanoclusters in catalysis as strong binding to the nanocluster surface tends to lead to ligand-*poisoned* nanoclusters (recall Scheme 5).

3.2.6. *Resorcinarenes*

Resorcinarene molecules have recently been employed as stabilizers for metal nanoclusters [162–170]. Resorcinarenes, also called calix[4]resorcinarenes or resorcinol-derived calix[4]arenes [171], are surfactants with macrocyclic headgroups, Fig. 4. Often, resorcinarenes have either thiols (as in Fig. 4) or hydroxy groups incorporated into the headgroup, and hence in their deprotonated form can be classified as steric (really, ligand) stabilizers. These resorcinarenes, with multiple adsorption points on the nanocluster surface, are believed to be more effective stabilizers than other surfactants with small, monodentate headgroups [163,167,168]. However, little direct evidence exists to validate this hypothesis. Resorcinarenes do display increased spacing between hydrocarbon chains relative to long, single hydrocarbon chain surfactants, which is claimed to result in improved steric repulsion between particles and reduced entropic cost of nanocluster stabilization through the need for fewer large resorcinarene molecules per nanocluster [162]. Nanoclusters with resorcinarene stabilizers are prepared by generation as aerosols [162,167], citrate reduction of the organometallic precursor [163,168], or thermolysis [165], followed by extraction into organic solutions containing resorcinarene molecules. In some cases, near-monodisperse 34 ± 2 nm Au nanoclusters were observed by TEM [162]. When chloride-containing organometallic precursors are used [163,168] it is again likely that the nanocluster's surface is passivated by at least some Cl^- as well as resorcinarene molecules, a point which remains to be experimentally investigated.

However, to date stabilization by resorcinarenes has only been demonstrated for Au and Co nanoclusters. Additionally, resorcinarene stabilization is insufficient to allow complete redissolution of isolated nanoclusters [165,168] indicating a failure in one of the key goals of nanocluster science [27], the synthesis of "bottleable" nanoclusters that can be made, stored in the solid state, then weighed out at any desired time later in any desired amount like other, well-established, optimum chemicals. Although one of the claimed benefits of using resorcinarenes as stabilizers is increased availability of catalytically active surface atoms, there are no reports of catalytically active nanoclusters stabilized by resorcinarenes. Accordingly, again missing is the needed comparison of the catalytic activity *per exposed metal* [149] to the most active nanoclusters, for example by the previously cited CS_2 poisoning method [149]. Comparisons of catalytic activity per exposed metal atom are needed for all future claims of high catalytic activity of any nanoclusters [149].

3.2.7. *Amines and phosphines*

Long-chain amines and phosphines provide another example of steric ("ligand") stabilization of nanoclusters. For example, amines and phosphines have been used in the preparation of Au [84], Ni [172], Ru [160], Co [173], and Pd [174] colloids. However, these stabilizers do not appear to be superior, since "superstructures" of colloids are often formed [160,174]. These "superstructures," upon inspection of the TEM micrographs, are really just agglomerates of smaller clusters. This extensive agglomeration indicates ineffective stabilization. Additionally, *none* of these studies performed the needed TEM controls of examining the precursor under the electron beam to check for colloidal formation and/or agglomeration during TEM analysis [49,51,52], controls especially important for lighter metals such as Ni and Co. Direct, *in situ* molecular weight measurements using ultracentrifugation [14] are needed to confirm or refute the presence of such "superstructures" in solution versus as an artifact of the TEM preparation or observation.

3.2.8. *Branched polymers*

Yet other examples of steric stabilization can be found in hyperbranched polymers such as aramids [175,176] and polyglycerols [177]. However, hyperbranched polymers such as polyglycerol have a less well-defined (e.g., when compared to dendrimers), and usually uncontrolled, structure. Nonetheless, polyglycerol stabilizers yielded Pd nanoclusters that were stable in solution for months and capable of catalyzing the hydrogenation of cyclohexene at a rate claimed faster than a commercial supported Pd/activated charcoal catalyst [177]. Unfortunately, again the needed catalytic rate *per exposed Pd* for each system, as required for a rigorous comparison of their activities, is not available [149]. Hence, the claim of a superior rate to the commercial Pd catalyst remains undocumented. Polyaramids were also used to stabilize Pd nanoclusters, yielding nanoclusters with an average diameter of 3.2 nm (no size distribution was given) [175]. Though catalytically active for the hydrogenation of a wide variety of olefins, TEM micrographs show that these nanoclusters are agglomerated [175]. Hence, branched polymers do not appear to be superior steric stabilizers.

3.2.9. *Summary*

In summary, steric stabilization of colloids and nanoclusters has proved useful since the 1940s [122,123], and will likely find continued utility in the future. However, finding the *optimum* steric stabilizer that yields compositionally well-defined, highly stable, isolable and redissolvable nanoclusters that retain high catalytic activity remains an important, unsolved problem.

3.3. *"Electrosteric"-combined DLVO-type electrostatic plus steric-stabilization*

In the literature, many authors have combined the two well-precedented modes of nanocluster stabilization into so-called "electrosteric" stabilization. Tracking down the origin and a clear definition of this term proved difficult. It is mentioned in a 1983 text [80] on the polymeric stabilization of colloids: however, in that text there are also several vague references to earlier use of "electrosteric" stabilization in biological systems. As the term "electrosteric" implies, this mode of stabilization is a combination of electrostatic stabilization (as described in DLVO theory) and steric stabilization. Electrosteric stabilizers have the potential to be superior for catalytic applications, as the combination of electrostatic and steric stabilization *may* mean that fewer equivalents of stabilizer per nanocluster are necessary for stabilization, *possibly* leaving more coordinatively unsaturated surface atoms available for catalysis. Note, however, that one weakness in the description of "electrosteric" is that there is neither a clear definition of an "electrosteric" stabilizer nor a cut-off as to when a stabilizer is large enough to be "electrosteric" versus a DLVO-type (electrostatic) stabilizer.

The first report on polyoxoanion-stabilized nanoclusters noted that the $P_2W_{15}Nb_3O_{62}^{9-}$ and associated $(Bu_4N)_9^{9+}$ stabilization of $Ir(0)_{\sim 300}$ nanoclusters was of apparently a novel type—a "combined high charge plus significant steric bulk present intrinsically" [14] within the (large, ca. 15 Å by 12 Å [27]) polyoxoanion and nine (large) Bu_4N^+ countercations (see p. 8342 elsewhere [14]). Since then, $P_2W_{15}Nb_3O_{62}^{9-}$ has been used to stabilize both Ir [6,9–12,14,78,79,178] and Rh [15,50,149] nanoclusters. Hence, it would be tempting to term these highly charged, sterically massive stabilizers as prototype "electrosteric" stabilizers.

A 2002 study employing the 5 criteria method found that the potentially "electrosteric" $P_2W_{15}Nb_3O_{62}^{9-}$ stabilizing anions (with Bu_4N^+ countercations), Fig. 5, were superior for the *formation* and *stabilization* of $Ir(0)_{\sim 300}$ nanoclusters, in comparison to $SiW_9Nb_3O_{40}^{7-}$, $C_6H_5O_7^{3-}$ (citrate), $[–CH_2–CH(CO_2^-)–]_n^{n-}$ (poly(acrylate)), OAc^-, $P_3O_9^{3-}$ (trimetaphosphate), Cl^-, or OH^-. Specifically, the results of the 5 criteria methods for $P_2W_{15}Nb_3O_{62}^{9-}$ were: (i) a high level of kinetic control during the nanocluster formation reaction, as reflected by a large value of $\sim 10^5$ for the k_2/k_1 ratio for autocatalytic growth (k_2) to nucleation (k_1); (ii) the formation of near-monodisperse nanoclusters as verified by TEM (often displaying a size dispersion of <14%, impressive for a self-assembly reaction involving >300 steps; for more details on nanocluster formation see reference [8] and earlier references therein); (iii) the ability to isolate (from solution) and bottle the nanoclusters for future use, the $P_2W_{15}Nb_3O_{62}^{9-}$ stabilized nanoclusters being taken to dryness and redissolved with no discernable agglomeration by TEM;[10] (iv) the catalytic activity of 2.2 mmol H_2/h at 22 °C and 40 psig H_2 of the isolated nanoclusters once redissolving them in solution with fresh substrate (in a separate preparation of $P_2W_{15}Nb_3O_{62}^{9-}$ stabilized, isolated, bottled, and redispersed $Ir_{\sim 2000}$ nanoclusters, 65% of the initial hydrogenation activity was retained [178]); and (v) a total catalytic lifetime in solution of 68,000 total turnovers (TTOs) of cyclohexene hydrogenation without the formation of visible bulk metal. In the case of $Ir(0)_{\sim 2000}$ $P_2W_{15}Nb_3O_{62}^{9-}$ and tetrabutylammonium-stabilized $Ir(0)_n$ nanoclusters, CS_2 poisoning studies show that of the ~31% out of the total ~2000 Ir(0) on the nanoclusters' surface, about 7–8% of that exposed Ir(0) is catalytically active [178]. A pictorial representation of $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion-stabilized nanoclusters is shown in Fig. 5.

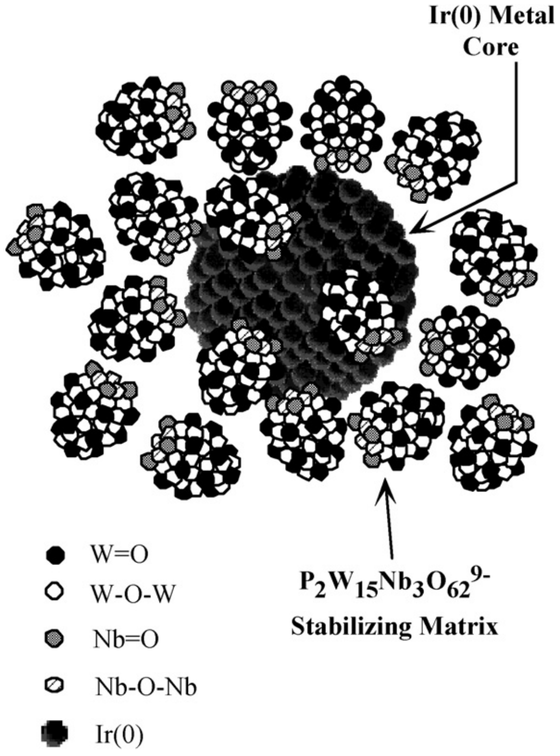


Fig. 5. Idealized, roughly to scale representation of a $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion and Bu_4N^+ stabilized $Ir(0)_{\sim 300}$ nanocluster. For the sake of clarity, only 17 polyoxoanions are shown and the Bu_4N^+ cations have been omitted. The polyoxoanions are of course actually coordinated to the $Ir(0)_{\sim 300}$ nanoclusters, although this is not illustrated in this particular representation. Reprinted with permission from Ref. [15]. Copyright 2001 American Chemical Society.

The case of $P_2W_{15}Nb_3O_{62}^{9-}$- and Bu_4N^+-stabilized Ir(0) nanoclusters is of special note as this system is one of the

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[10] The fact that these nanoclusters can be taken to dryness and subsequently redispersed indicates that they lack a so-called critical coagulation constant (ccc). Classical colloids possess a ccc: upon adding electrolyte (thus compacting the protective electrical double layer (Debye layer)), the colloids become unstable and precipitate from solution. The lack of a ccc in the case of selected nanoclusters, for example the above-mentioned $P_2W_{15}Nb_3O_{62}^{9-}$ and tetrabutylammonium-stabilized nanoclusters, indicates that they possess an unusual stability with respect to most classical colloids [9].

few *compositionally well-defined* nanocluster systems. The nanocluster composition was established by full elemental analysis and analytical ultracentrifugation molecular weight measurements [14]. Additionally, electrophoresis measurements demand that the 9^- anions are coordinated to the surface of the neutral Ir(0) core [14]. These nanoclusters have a balanced stoichiometry of formation [14], have been scaled up [178], are isolable and "bottleable" [9,10], and have had the number of active sites determined by CS_2 poisoning [178]. More compositionally well-defined nanocluster systems such as this system and the others listed in Table 1 are needed for nanocluster science to proceed more efficiently.

Other groups have also picked up the idea of "electrosteric" polyoxoanion stabilizers [179–181]. However, there remains confusion about claims whether or not non-basic polyoxoanions such as $PW_{12}O_{40}^{3-}$, $SiW_{12}O_{40}^{4-}$, or $P_2W_{18}O_{62}^{3-}$ are stabilizers (as their Bu_4N^+ salts) [14]. Note that these classic types of polyoxoanions are weakly basic at best (they formally have zero surface-charge density as rewriting these anions as $(PO_4^{3-})(W_{12}O_{36}^{0})$, $(SiO_4^{4-})(W_{12}O_{36}^{0})$, and $(PO_4^{3-})_2(W_{18}O_{54}^{0})$ shows). Hence, these classic types of polyoxoanions have little surface anionic charge density at least formally, their conjugate acids are very strong acids [182], and they have been tested and found *not* to stabilize $Ir(0)_n$ nanoclusters [14]. This "non-stabilization" result has been repeated recently for $PW_{12}O_{40}^{3-}$ and $P_2W_{18}O_{62}^{3-}$ in acetone with the known nanocluster precursors $[(1,5\text{-COD})Ir(CH_3CN)_2][BF_4]$ and Pd_2(bis-dibenzylidene acetonate)$_3$ with the finding that the original result [14] is repeatable: bulk metal, not well-stabilized nanoclusters, are the end result [14]. It is not clear why others continue to claim that these weakly basic polyoxoanions are good stabilizers [181]. Studies of potentially tetradentate-oxygen ligand stabilizers $PW_{11}O_{39}^{7-}$ and $P_2W_{17}O_{61}^{10-}$ have been reported [184–188] and are presently being investigated by the 5 criteria method [189]. These polyoxoanions do have surface oxygen basicity and should be decent, perhaps even superior, stabilizers.

Returning to the subject of what is and is not an "electrosteric" stabilizer, and also given that DLVO theory treats anions as point charges, anything larger than a point charge (i.e., *everything*) would, therefore, be classified as an electrosteric stabilizer. The main problem with the term "electrosteric," then, is its ill-defined nature and seemingly too-broad definition. Whether or not the term "electrosteric" should remain in the literature as a mode of nanocluster stabilization remains to be seen—however, due to the widespread use of the term, we felt it prudent to cover the term "electrosteric". On reflection, we do recommend the use of "electrosteric stabilizers", but suggest that the term be reserved for examples that have both multiple charge (i.e., $\geq 2^-$) and steric bulk in one dimension at minimum of one quarter the size of the nanocluster (e.g., a 5 nm electrosterically stabilized nanocluster would require a stabilizer of $\geq 2^-$ with one dimension of the stabilizer being ≥ 1.25 nm). $P_2W_{15}Nb_3O_{62}^{9-}$ stabilized 2.0 nm $Ir(0)_{\sim 300}$ nanoclusters clearly fit, then, this definition of electosterically stabilized nanoclusters.

4. Other possible modes of nanocluster stabilization

In the literature, there are several postulated mechanisms for nanocluster stabilization that are not addressed by electrostatic, steric, or electrosteric stabilization. Most of these claimed stabilization schemes need to be more carefully evaluated. Again a recurring theme in the following examples – indeed, in almost all of the nanocluster stabilization literature except for a handful of important papers (see for example references [14,15,84,85,88] in Table 1) – is the need for *compositionally well-defined* nanoclusters so that the putative stabilizers *that are actually present* are known. Also again, *in situ* nanocluster solution "stability" is often assessed only by TEM, an *ex situ*, solid state technique. Much greater use of (i) the 5 criteria method of evaluating stabilizers [9,10], (ii) an agglomeration-based, quantitative kinetic method for evaluating stabilizers [75], and (iii) *in situ* techniques such as XAFS and SAXS are needed prior to any claim that a superior stabilizer has been discovered.

4.1. Putative cation-only stabilization

A literature hypothesis is that modern transition-metal nanoclusters can be stabilized by only tetraalkylammonium *cations*[11] [38,161,190]. Notably, a widely cited *Science* paper [190] assumes that R_4N^+ cations are directly coordinated to Ag particle surfaces (see Footnote 11). However, cationic stabilization is counterintuitive, given that positively charged cations (with no free electron pair to serve as a ligand!) should not be attracted to the *electrophilic* nanocluster surfaces (as posited and pictorially shown in Ref. [191]; see also Fig. 6 below), a point that has been corrected in the literature [27]. Despite this correction, there are many reports of nanoclusters prepared in the presence of tetraalkylammonium halides wherein the nanoclusters are judged to be stable and the *cation* is claimed as the stabilizer [38,39,190,191,192]. In many of these studies [38,39,190,192], the authors fail to consider the effects of the *halide* (present in 5–6% by elemental analysis of the nanoclusters after being taken to dryness [38]), halide which DLVO theory predicts will be drawn to the (electrophilic) nanocluster surface [94]. Following a correction of this [9,27], in more recent contributions, it has been recognized that in the case of Pd colloids prepared in the presence of long-chain $[R_4N][Cl]$ com-

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[11] The belief that the cationic component of a surfactant is the stabilizer appears to have some roots in a 1979 *J. Am. Chem. Soc.* paper [127]. In that paper, the authors report "for the first time that a surfactant acts as a protective agent for metal platinum". However, significant sources of Cl^- exist therein from both $PtCl_4$ and the cetyltrimethylammonium chloride surfactant employed. The myth that R_4N^+ cations may be directly coordinated to the nanocluster surface is traceable to a 1988 paper employing surface enhanced Raman scattering on poorly characterized Ag colloids (J. Weisner, A. Wokaun, H. Hoffmann, Prog. Colloid Poly. Sci. 76 (1988) 271). While that paper implies that the long-chain amines are present on the Ag surface, the authors recognize that the binding of a *cationic* amine to a *cationic* Ag^+ surface "must imply the intermediacy of . . . the Br^- counteranion." Unfortunately, others [190] incorrectly cite this paper as providing evidence for R_4N^+ coordination to a nanocluster surface, apparently since they just refer to the misleading figure (Fig. 3 of the Prog. Colloid Poly. Sci. paper cited above) rather than carefully reading the text noted above.

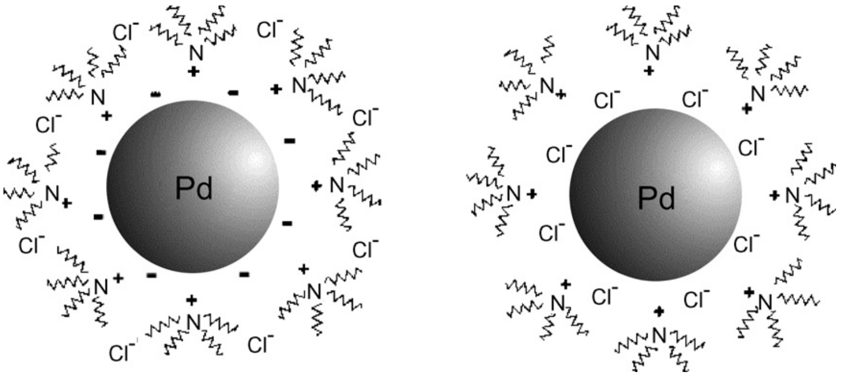


Fig. 6. Two literature representations of nanocluster stabilization by bound anions plus surrounding R_4N^+ surfactant [193]. In the figure on the left, the nanocluster is assumed to bear negative charge [193]. In the figure on the right, the neutral metal core is surrounded by Cl^- anions that provide DLVO-type stabilization [193]. Also of note in this figure and others by the same group is the incorrect, square-pyramidal representation of the four alkyl ligands on the ammonium cation. Reprinted from Ref. [193] with permission from Elsevier.

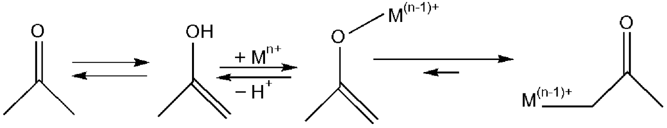
pounds that Cl^- is "the more appropriate stabilization mode" [193,194] as detailed in the right-hand side of Fig. 6.

In a similar case, the hypothesis that the cation is the nanocluster stabilizer is paired with an *assumption* that the surface of Group 6–11 nanoclusters bore negative charge after being reduced by tetraalkylammonium hydrotriorganoborates [38]. However, elemental analysis of a sample of a putatively tetraoctylammonium-stabilized palladium nanoclusters shows 3.98% Br^- is present [38]. With a mean particle size of 4.8 nm [38], approximately 26% of the Pd atoms are on the surface.[12] Back-of-the-envelope calculations indicate this particle size and Br^- content would yield approximately 1 Br^- atom for every 3 Pd surface atoms, which is probably more than sufficient to provide electrostatic stabilization. The evidence (NMR, MS, and elemental analysis) indicating of the presence of the tetraoctylammonium cation in the isolated material is consistent with the multi-layer of ions surrounding the nanocluster as *predicted by DLVO theory* [94]. In later papers by the same group, post the correction provided elsewhere [9,27], the stabilizers is assigned as "$R_4N^+X^-$", thereby acknowledging the role of the halide [195].

DLVO theory predicts that large cations, such as tetraalkylammoniums, should have a contribution to the stability of electrostatically stabilized systems by expanding the diffuse layer of ions around the colloid and hence increasing the thickness of the Debye layer [94] as well as their natural steric effect. However, and again as DLVO theory predicts, the *anions* should be the primary source of stabilization for the electrophilic nanoclusters. The cationic stabilizer assumption has been propagated through the literature from its apparent beginning with the miscited Ag surface-enhanced Raman scattering (SERS) paper [190], even appearing in electrochemistry textbooks [196]. As argued elsewhere, "propagation of this apparent myth should be stopped until, and unless, direct, compelling evidence for a non-anion-mediated, direct R_4N^+ to nanocluster interaction is forthcoming" [197].

4.2. Putative solvent-only stabilization

Another putative type of stabilization in the recent literature is "solvent-only" stabilization [39,198–206]. This type of stabilization is in theory attractive, with *potential* benefits including availability of surface sites for catalysis in the absence of strongly coordinated ligands, simplicity of reaction conditions, and avoidance of surface contamination. However, there is no clear source of stabilization in claimed "solvent-only" stabilized systems, as by definition such "solvent-only" systems must lack the ions necessary for DLVO-type stabilization and also have no bulky, tightly bound ligands that would qualify as steric stabilizers. As in the case of claimed cationic stabilization discussed above, in "solvent-only" stabilization *halides are often present* [198,201] so that the alternative hypothesis of halide-mediated DLVO-type stabilization has, again and unfortunately, not been disproved or, often, *even considered*. Additionally, there are frequently other nanocluster stabilizers and/or contaminants present, such as acetate [202], hydroxide [201], alcohols [199,202], water [202], and other species [200,205].[13] In fact, in one study it was noted that a "passivating oxide layer" was



Scheme 6. Potential stabilization of M(0) species by ketones.

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[12] The approximate number of surface atoms was calculated with the formula based on the "magic number" nanoclusters [14]. A 4.8 nm cluster contains approximately 3937 Pd atoms, which is close to the 10-shell magic number of 3871 atoms. The number of surface atoms is calculated using the equation $y = 10n2 + 2$ (where y is the number of surface atoms and n is the number of shells in the cluster). From this equation, 10 shells have 1002 surface atoms and 1002/3871 = 26% surface atoms.

[13] In these final two cases, the only solvents that yielded nanoclusters were ketones. These ketones may participate in a limited stabilization by undergoing keto-enol tautomerism followed by deprotonation to yield, initially, an alkoxide stabilizer which may then undergo further conversion as in Scheme 6 for the specific example of acetone. Interestingly, an impurity in acetone has been shown to lead to an increased rate of hydrogenation catalytic activity for $Ir(0)_n$ nanoclusters, but remains unidentified despite considerable effort to uncover its identity (see p. 10–13 of the Supporting Information elsewhere [14]).

detected by both X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) [199], this oxide layer in our view likely being the main source of the nanocluster stability.[14] Hence, it is likely that such nanoclusters are not solely "solvent-only" stabilized. They are likely often anion, oxide coating [207–213], or otherwise stabilized. Note in this regard, at least for small organometallic clusters, "solvent-only" clusters are unknown: that is, "$Ir_4(solvent)_{12}$", analogous to the well-known, stable, and soluble $Ir_4(CO)_{12}$, does not exist at least at present as even a meta-stable molecule, although $M_4H_4(stabilizer)_n{}^{x+/0/x-}$ clusters appears to be a new, important finding in (sub) nanocluster chemistry and catalysis [72].

As an example of "solvent-only" stabilization, putatively THF-stabilized "$Ti(0)_n$" nanoclusters were prepared by $K[BEt_3H]$ reduction [198]. However, the possibility of stabilization by Cl^- was not considered despite a Cl content of 8.5% by elemental analysis [198]. Also, KCl was observed in the X-ray diffraction pattern of the isolated metal colloid. In addition, the use of $BH_4{}^-$ as a reductant invariably leads to the presence of a few percent of B in the resultant nanoclusters (for example, Zr colloids prepared as part of the abovementioned study contained 3.7% B [198]). Despite this evidence, the authors concluded that stabilization of the Ti nanoclusters resulted from a combination of coordinated THF and surface hydrides. Again, the problematic trend of interpreting one's data only in terms of one's original hypothesis is apparent, as well as the pattern of a lack of disproof of alternative hypotheses that is required for good, efficient science [81]. Also, the need for *compositionally well-defined* nanoclusters is once again re-emphasized: a complete understanding of the composition of one's nanoclusters *must* be in hand before one can postulate all possible alternative hypotheses [81] on how the nanoclusters might be stabilized, followed by the necessary attempts at disproof of each of those alternative hypotheses. What's left, often necessarily interpreted with the aid of the conditional exclusion we call "Ockham's Razor" [214] yields, then, the experimentally supported stabilization modes(s).

Chaudret and co-workers have also reported several cases of "solvent-only" stabilized nanoclusters [199,203]. One clever design feature in these systems is that they are prepared with the anion-free precursor [Ru(1,5-COD)(COT)] (where COT = cyclooctatriene) in THF plus varying, but predetermined, equivalents of MeOH. The use of this precursor excludes from the start the alternative hypothesis that anions like Cl^- are contributing to the stability of the system. However, employing alcoholic solvents such as methanol leads to the possibility that the alcohol can serve as both the reductant and subsequently, a possible MeO^- stabilizer. Instead, ill-defined stabilizing "nanoreactors", "vesicles", or "pockets" are hypothesized to be formed with cyclooctane (as a byproduct of the decomposition of the precursor) in mixed ROH/THF solvents, all without compelling evidence [199,203]—the main pieces of evidence again being based on TEM and other *ex situ* solid-state techniques. Note also here that another alternative hypothesis not ruled out is that the solvent has reacted, for example through a ring-opening of THF at the active metal surface which could at least conceivably yield an oligomeric/polymeric THF-product based stabilizer (i.e., and then polymer, rather than "solvent-only", stabilized nanoclusters). Other alternative hypotheses as to the source of the stabilization may be possible as well and would, then, also require disproof.

Another precursor that appears ideal for studying solvent-only stabilization is $Pd_2(dba)_3$ (where dba is dibenzylidene acetonate) [215]. However, elemental analysis of isolated nanoclusters prepared from this precursor shows >41% C (relative to the entire mass of the sample) and the XPS C 1s spectrum indicates the presence of "amorphous (graphitic) carbon" on the surface of the nanoclusters [215]—a potential if not obvious stabilizer. In any event, the surface layer of carbon means the nanoclusters prepared in this study, too, are not truly "solvent-only" stabilized.

One paper testing 7 alternative hypotheses for solvent-only stabilized nanoclusters has appeared [97]. By using the system $[(1,5\text{-COD})Ir(CH_3CN)_2][BF_4]$ with only the weakly coordinating $BF_4{}^-$ anion in five different solvents, and by ensuring the absence of O_2, H_2O, ROH, and Cl^-, the "solvent-only" stabilization hypothesis was subjected to its first more rigorous test via the 5 criteria method. The main findings of that study are that: (i) even high donor number solvents alone do not provide enough stabilization to allow for the formation of "solvent-only" stabilized nanoclusters; (ii) traditionally weakly coordinating anions such as $BF_4{}^-$ yield to solution meta-stable nanoclusters in high dielectric constant solvents, consistent with DLVO theory; and (iii) exposure to O_2 or the strong ligand pyridine are needed to attain long-term (>2 weeks) solution stability. In short, putative "solvent-only" stabilized nanoclusters appear to be another, now de-bunked [97] myth of the nanocluster area.

4.3. Room-temperature ionic liquid stabilization

One additional postulated mode of nanocluster stabilization is room-temperature ionic liquid (IL) stabilization [216–221]. These low vapor pressure (but distillable [222]), highly polar, viscous solvents have received much recent attention in the literature [223–226], with a plethora of reactions having been carried out in IL media as covered in several review articles [227–229]. Recently, there have been reports of catalytically active nanoclusters suspended in ionic liquids [216–221]. However, as in the organic "solvent-only" stabilized cases above, these nanocluster/IL systems are frequently contaminated by halides (not only from halogenated nanocluster precursors [216] but from the preparation of the ILs themselves from imidazolium *halide* precursors [230]), thus leading to the possibility of halide stabilization even though IL stabilization is claimed. In addition,

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[14] The O_2 sensitivity of nanoclusters has been little studied. However, recent work in showed that Ir(0) nanoclusters stored in the drybox display a greater-than-expected, *apparent* oxygen sensitivity, losing almost 90% of their activity during the course of a year [178]. Of note is that nanoclusters of all metals are expected to show much more air sensitivity than their bulk metal counterparts due to the nanoclusters' higher surface area, their higher energetic nature (i.e., their less negative $\Delta H_{\text{formation}}$), and, hence, their greater reactivity towards ligands such as O_2 [178].

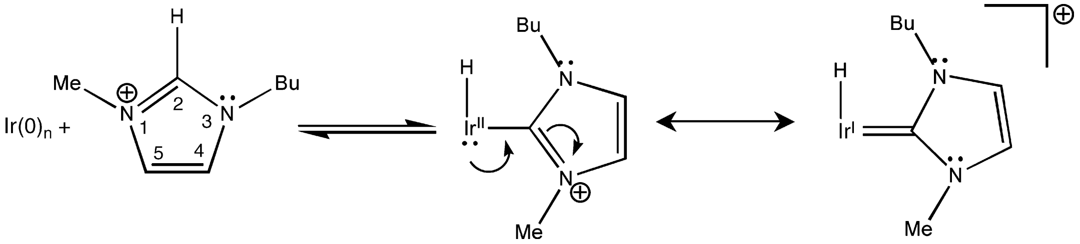

Fig. 7. Proposed mechanism for the formation of *N*-heterocyclic carbenes in the presence of nanoclusters (showing only one resonance form explicitly and omitting the anion for clarity), supported by H/D exchange studies which show D exchange in the C_2-H (and other [241]) positions of the imidazolium cation.

hygroscopic ILs have to be carefully dried before use to avoid surface contamination of the nanoclusters by water, hydroxides or oxides. The amount of halide present in ILs and on the resultant nanoclusters is rarely quantified, and these halide impurities can have detrimental effects on the ILs themselves (such as increasing the IL density and /or viscosity, or poisoning heterogeneous catalysts suspended in ILs [231]). The present best method used to quantify the halide concentration in ILs, ion chromatography [231], showed that the difference in Cl^- concentration in two [bmim][BF_4] samples from different sources to be 12.6 ppm versus 228 ppm: note the 18-fold difference in Cl^- concentration [232]. A Cl^- content of 228 ppm corresponds to approximately 8.4×10^{-3} M; hence, for a nanocluster sample such as $Ir_{\sim 300}$ nanoclusters [14] which have ~50% of their atoms on the surface, a 228 ppm Cl^- contamination of the IL leads to *approximately 12 Cl^- atoms per surface Ir atom*! Such high concentrations of chloride indicate that DLVO-type stabilization by chloride is a plausible – but untested – alternative hypothesis to that of the IL being the nanocluster stabilizer.

As is the case for "solvent-only" stabilized nanoclusters, there is no precedented mode of stabilization for transition-metal nanoclusters in ILs unless the weakly coordinating anions [233] that comprise half the composition of the IL (typically BF_4^-, PF_6^-, and $N(SO_2CF_3)_2^-$) are involved. Contributions to stability by one of these anions is consistent with the finding that BF_4^- can contribute to the stability of transition-metal nanoclusters in high dielectric constant solvents [97,183,105] (the dielectric constant of ILs remains somewhat controversial, however [234]). Additionally, Dupont et al. recently reported that PF_6^- from [bmim][PF_6] was found on a Pt(0) nanocluster surface by XPS [235]. This further supports the hypothesis that even weakly coordinating anions can contribute to the stability of transition-metal nanoclusters [97] in organic solutions or in ILs.

Of note here is that the literature reveals the "non-innocence" of ILs in the presence of transition metals. Specifically, there is growing precedent for oxidative addition to the C(2)–H bond of imidazolium cations to form a M(H)(*N*-heterocyclic carbene) [236–240]. The "non-innocence" of ILs in *nanocluster* formation and stabilization was recently investigated [241]. It was found that even under the mild conditions of 22 °C and 40 psig H_2, the oxidative addition and formation of *N*-heterocyclic carbenes from the imidazolium component of the IL was detectable by H/D exchange studies under D_2, Fig. 7. There *N*-heterocyclic carbenes are, then and in addition to the BF_4^-, another source of potential nanocluster stabilization in IL solvents [241]. Additionally, the *N*-heterocyclic carbenes derived from just 1 equiv. of imidazolium-based IL have been shown to poison ~90% of the catalytic activity of $Ir(0)_n$ in acetone [93].

4.4. Low concentration kinetic stabilization towards agglomeration

Since agglomeration is a bimolecular phenomena (i.e., the $\mathbf{B}+\mathbf{B} \rightarrow \mathbf{C}$ and $\mathbf{B}+\mathbf{C} \rightarrow 1.5\mathbf{C}$ steps in the four-step mechanism, Scheme 3), low concentrations of nanocluster can have long catalytic lifetimes due to the reduced probability of diffusional agglomeration. Accordingly, low concentrations of poorly stabilized – but thus unpoisoned/unligated and highly active nanoclusters – can serve as very active catalysts. This point is little appreciated. This kinetic stability as a function of solution concentration is a key part of the "Is it homogeneous or heterogeneous catalysis?" question dealt with elsewhere [242].

5. Summary and conclusions

The major findings of this review are as follows:

- Prior literature methods for ranking nanocluster stabilizers are dated and inadequate. These studies are 41 and 105 years old [42,44] and apply only to gold colloids prepared in water. Additionally, they are far too qualitative to be useful to modern nanocluster science. A plasmon-resonance method for the properly chosen and prepared Au, Ag, or Cu nanoclusters is conceivable, however, and is under a collaborative investigation [47].
- A method of ranking nanocluster stability by quantitating the temperature-induced nanocluster agglomeration rate constants k_3 and k_4 (Schemes 2 and 3) is now available [75].
- The five criteria developed in 2002 [9] represent an imperfect, but presently one available stride, towards quantitating both nanocluster formation and stabilization. Of these five criteria, four are quantitative. The five criteria are applicable at least in theory to all transition-metal nanoclusters in all solvents. In practice, however, application of the five criteria is possible only for relatively stable nanoclusters, since four of the five criteria – notably all of the criteria that measure stability – are non-quantifiable for unstable, non-isolable nanoclusters. However, this feature in itself is useful as it makes clear which

stabilizers are even *worth ranking* en route to identifying the top stabilizers. The five criteria have led to a ranking of anions [9–11], including the halides [183], testing of the effects of solvent and weakly coordinating anions [97], five different polymers [105], and 1,3-substituted imidazolium ionic liquids [241].

- There are two fundamental modes of nanocluster stabilization: electrostatic and steric. Additionally, the term "electrosteric" stabilization is commonly used to describe what authors consider a combination of the two main stabilization modes. Herein, we propose a semi-quantitative definition for an "electrosteric" stabilizer: those entities which possess both multiple charge ($\geq 2^-$) and steric bulk at minimum of roughly one quarter the size of the nanocluster in one dimension.
- Failure to determine the true nanocluster composition is a common denominator in the literature – *the* primary problem in identifying even the potential stabilizers which are present, much less which is the dominant, true source of any observed stabilization. For example, in a recent review titled "Recent Advances in the Liquid-Phase Syntheses of Inorganic Nanoparticles" [5] which cited 668 references, *the composition of each class of nanoclusters was never mentioned*. Instead, the claimed stabilizing agents were tacitly assumed to be correct without consideration of other stabilizing entities present in the solution. Note that given the lack of quantitative methods to measure stability and thereby rank stabilizers, it follows that much of the information regarding the nature of the stabilizer is on shaky ground.
- Hence, there exists a great deal of confusion in the nanocluster literature with respect to the nature of the true stabilizer in a given system. "Stability" is far too often claimed based on a few *ex situ* methods such as TEM images, images of course of the solid state, not of the desired solution sample. Several "non-classical" types of stabilization have been proposed based on such TEM evidence (only), although many of these claims are probably wrong or at least suspect if one realizes that the *composition* of the nanocluster system is often unknown. The lack of even formation of, much less disproof of, alternative hypotheses as to the true mode of stabilization is rampant in the nanocluster literature—a literature propelled too fast, too far, by a single, "too-sensitive" technique, TEM. Much greater use of *in situ/operando* methods of assaying nanocluster stability are needed (i.e., determination of the rate constants k_3 and k_4 [75], use of the 5 criteria method [9], and so on). Better science, consisting of the disproof of multiple alternative hypotheses [81], is badly needed in this area. At a minimum, seeing if the nanoclusters are stable enough to be taken to dryness, then redissolved without forming bulk metal, is a recommended test of stability that is one key part of the 5 criteria method.
- A "7 criteria method", that is the existing 5 criteria plus measurement of k_3 and k_4 agglomeration rate constants, is a needed next step in evaluating nanocluster stabilizers.
- Nanocluster science will not be able to move forward efficiently until stabilization is better understood and more often quantified. Doing so will greatly simplify the current "dizzying variety" [5] of claimed nanocluster stabilizers into a few preferred anions, solvents (e.g., propylene carbonate [39,97]) and steric stabilizers.

In short, it would be fair to say that reliable, quantitative studies of how nanoclusters of known composition are stabilized are just beginning. In one sense, we are only a bit past where a 1996 book chapter on "colloidal organometallic catalysis" noted we were[15] [243]. It is hoped that the present critical review will serve to expedite the needed studies as well as all the exciting science and expected important applications of isolable, compositionally well-defined transition-metal nanoclusters.

Notes added in proof

A *Nature* paper measures the electrophoretic mobility by laser Doppler velocimetry of a series of Au, Ag, Pt, PbSe and other nanoclusters [244] and finds, significantly, that the net charges on the nanoclusters *are not high*—consistent with the early report by Turkevich cited in the main text [29b]. Instead, they are *always within −2, −1, 0, or +1 for the systems studied* (the +1 being for a PbSe/RCO_2H system), charges that can be changed by the surfactants/ligands and their amounts which are present [244]. This in turn indicates that even relatively small net charges must be what are providing considerable DLVO-type stability, although this central hypothesis for nanocluster stabilization merits further experimental scrutiny.

A careful XAFS/TEM study by Menard et al. [245] shows how the use of high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) in conjunction with XAFS can identify compositions to the precision of $Au_{13\pm3}$ or $Au_{\sim180\pm116}(SR)_{\sim40}$, a non-trivial accomplishment. More widespread use of these methods in nanocluster science is to be encouraged.

Finally, a study decomposing the alkyl-phenyl diazonium salt $C_{10}H_{21}$-C_6H_4-$N_2^+BF_4^-$ onto Au or Pt nanoclusters yields R-C_6H_4-surface-functionalized, isolable and chromatographable nanoclusters [246]. Unfortuanately, these novel R-C_6-H_4-functionalized nanoclusters were, apparently, prepared under O_2 so that some oxide coating is also probable; also lacking are a balanced reaction for the synthesis, any compositional information of the nanoclusters, and any quantitative idea of the amount of R-C_6-H_4 on the surface. These omissions mean that this interesting initial communication will require a subsequent full paper report to become more useful to the nanocluster community.

Acknowledgement

This work was supported by DOE grant DE-FG02-03ER15453.

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[15] Therein, G. Schmid noted that "Little is known as to how conventional ligands and other ingredients stabilize metal colloids during a given "homogeneous" process." This statement appears equally true today, even after considerable effort in the area of nanocluster science during the last decade.

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