A perspective on nanocluster catalysis: polyoxoanion and $(n\text{-}C_4H_9)_4N^+$ stabilized Ir(0)$_{\sim 300}$ nanocluster 'soluble heterogeneous catalysts'

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Abstract

Following a review of the background terms, definitions and key literature necessary to understand the rapidly developing and promising area of nanocluster catalysis, the recent report of polyoxoanion-stabilized Ir(0)$_{\sim 190-450}$ (hereafter Ir(0)$_{\sim 300}$) nanocluster catalysts is reviewed. Specifically, the experimental observations relating to three principle questions concerning these soluble-oxide-supported, Ir(0)$_{\sim 300}$ nanocluster catalysts are reviewed: (i) their catalytic activity (in a prototypical structure-insensitive reaction, cyclohexene hydrogenation); (ii) their lifetime; and (iii) their thermal stability, each in direct comparison to three established heterogeneous Ir(0) catalysts [7.9% dispersed 1% Ir(0)/γ-Al$_2$O$_3$, Exxon's 80% dispersed 1% Ir/η-Al$_2$O$_3$, and a low surface area Ir(0) precipitate]. In addition, observations of W^{VI} to W$^{V\cdot}$ reduction of the polyoxoanion by Ir(0)$_{\sim 300}$ and H$_2$ are summarized, results which provide the first soluble-oxide version of the well known spillover of hydrogen in heterogeneous catalysis.

Keywords: Review; Transition metal nanoclusters; Polyoxoanion-stabilized clusters; Polyoxoanions; Homogeneous catalysis; Heterogeneous catalysis; Soluble metal-particle catalysis; Nanocolloids; Hydrogenations; Catalytic activity; Catalytic lifetime; Thermal stability; Hydrogen spillover

1. Introduction

Polyoxoanion [1]-supported organometallics [1] [2–5], such as the prototype iridium(I) complex [4] $(Bu_4N)_5Na_3[(1,5\text{-cyclooctadiene})Ir \cdot P_2W_{15}Nb_3O_{62}]$, **1**, Fig. 1, are soluble analogs [1]c of solid-oxide-supported, atomically dis-

persed, [2] heterogeneous transition-metal catalysts. Complex **1** and its congeners are of considerable interest as discrete, soluble-oxide-supported analogs of such heterogeneous catalysts,

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[1] Organometallic derivatives of polyoxoanions, unknown until a decade ago, are now relatively common. Still in their infancy, however, are studies of their reactivity, catalysis, or mechanisms [2]f.

[2] (a) To date, no *bona fide* example of a *stable*, atomically dispersed, oxide-supported, *zero-valent* transition metal heterogeneous catalyst exists, a point made previously by Boudart [13]d. (b) Note that our results show that even the very basic $P_2W_{15}Nb_3O_{62}^{9-}$ oxide–support system is unable to immobilize (i.e., to site-isolate) a single Ir(0) atom, since $[(1,5\text{-COD})Ir(I) \cdot P_2W_{15}Nb_3O_{62}]^{8-}$ plus H$_2$ forms Ir(0)$_{\sim 300}$, and not $\cdot$Ir(0)$\cdot P_2W_{15}Nb_3O_{62}^{9-}$', which remains unknown. This finding is arguably the most definitive evidence available that single, *zero-valent* metal atoms are not stable on at least basic-oxide supports [13]d.

and they have already served as precatalysts for new and reactive catalyst compositions [5]. In addition, **1** is among the very few oxide-supported catalyst precursors whose structures, and thus whose mechanisms, can more easily be fully characterized at the *atomic* level [4], issues of fundamental significance to catalysis. For this reason, polyoxoanion-supported homogeneous catalysts have been under development and investigation in our laboratories for more than a decade [3–8].

In 1991 we described the reaction of **1** with O_2 to give rise to the first polyoxoanion-supported oxidation catalyst [5]. Subsequent mechanistic investigations [5]c confirm that the resultant catalyst contains oxidized Ir bonded firmly to the basic $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion.

Rather different is the behavior of **1** under H_2. A second, new composition of matter is formed, polyoxoanion- and Bu_4N^+-stabilized, 20.3 ± 2.8 Å $Ir(0)_{\sim 190-450}$ (hereafter $Ir(0)_{\sim 300}$) nanoclusters, visualized by TEM in Fig. 2 [5–8]. These new catalytic materials have been extensively characterized by TEM, electron diffraction, electrophoresis, elemental analysis, ultracentrifugation MW determination, and IR and UV-visible spectroscopy [6,7]. Their polyoxoanion component is without precedent in any previous type of nanocluster or colloid.

These $Ir_{\sim 300} \cdot$ polyoxoanion-stabilized nanoclusters are in one sense colloid-like, but are *very different in five important and advantageous ways*: (i) they are formed with a relatively narrow ($\pm 14\%$) size distribution; (ii) they are polyoxoanion-stabilized—that is, in intimate contact with, and thus 'loosely supported by', the soluble polyoxoanion oxide [6,7], an oxide material of *exactly known structure* (recall Fig. 1) [4]; and (iii) they are sufficiently stabilized by the polyoxoanion and its associated Bu_4N^+ counter ions that they *can be isolated and stored as a bottled reagent* [6–9]—*yet they retain a high catalytic activity!* This combination of isolability, yet high catalytic activity *and* stability in solution under catalytic conditions, is what distinguishes these and one other nan-
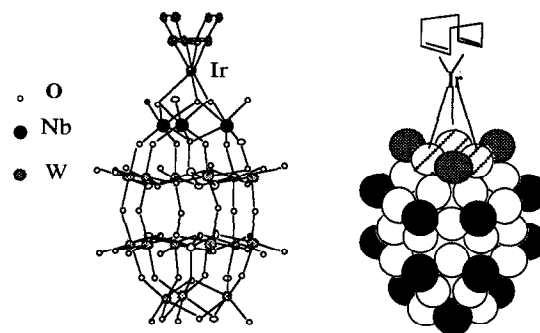

Fig. 1. Ball and stick (leftmost) and space-filling (rightmost) representations of $(Bu_4N)_5Na_3[(1,5\text{-COD})Ir \cdot P_2W_{15}Nb_3O_{62}]$, **1**. The Bu_4N^+ and Na^+ counterions have been omitted for clarity. In the space-filling representation the black circles represent terminal M=O oxygens, whereas the open, white circles represent M–O–M bridging oxygens.

ocluster ($Pd_{\sim 570}$, vide infra) from all others, as will be documented in greater detail herein. In addition, even (iv) the complete molecular composition of these nanoclusters has been unequivocally determined, a situation virtually unknown in traditional metal-colloid chemistry. Having an isolable nanocluster of established molecular formula means that these $Ir(0)_{\sim 300} \cdot$ polyoxoanion nanoclusters can be weighed out and redissolved (with little detectable aggregation, by TEM), and thus studied later at one's convenience. *This combination of isolability, known molecular formula, as well as the retention of catalytic activity is little precedented in nanocluster catalytic science*, as the review of the most recent nanocluster catalysis literature herein will document. This combination of properties means, in turn, that the catalytic reactions and mechanisms of the $Ir(0)_{\sim 300} \cdot$ polyoxoanion nanoclusters can be studied in detail and in solution, analogous to any other homogeneous catalyst, via solution kinetics [3] plus the full arsenal of powerful, solution-spectroscopic probes.

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[3] Note that there would still be an issue when studying non-monodisperse (or possibly even near monodisperse) samples, that one is seeing an average response to a given physical property. However, this situation would be no different than that with a traditional, non-monodisperse heterogeneous catalyst.

Scrutiny of the transition metal nanocluster literature [6–17] (provided in the sections that follow) reveals that these $Ir(0)_{\sim 300}$ nanoclusters are one of the two best *compositionally*—but not the best structurally, vide infra—characterized *catalytic* transition metal nanoclusters known to date, with an *average* composition of $[Ir(0)_{\sim 300}(P_4W_{30}Nb_6O_{123}^{16-})_{\sim 33}]$ $(Bu_4N)_{\sim 300}Na_{\sim 233}$. (The range of $Ir(0)_{\sim 190-450}$ nanoclusters present and depicted in the bar graph in Fig. 2b is referred to herein, for the

Fig. 3. Idealized, roughly-to-scale representation of a $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion and Bu_4N^+ stabilized $Ir(0)_{\sim 300}$ nanocluster, $[Ir(0)_{\sim 300}(P_4W_{30}Nb_6O_{123}^{16-})_{\sim 33}]$ $(Bu_4N)_{\sim 300}Na_{\sim 233}$. The Ir(0) atoms are known to be cubic-closed packed as shown [6]. For the sake of clarity, the polyoxoanion is shown in its monomeric, $P_2W_{15}Nb_3O_{62}^{9-}$ form (and not as its Nb–O–Nb bridged, anhydride form), only 17 polyoxoanions are shown, and the ~ 300 Bu_4N^+ and ~ 233 Na^+ cations have been deliberately omitted.
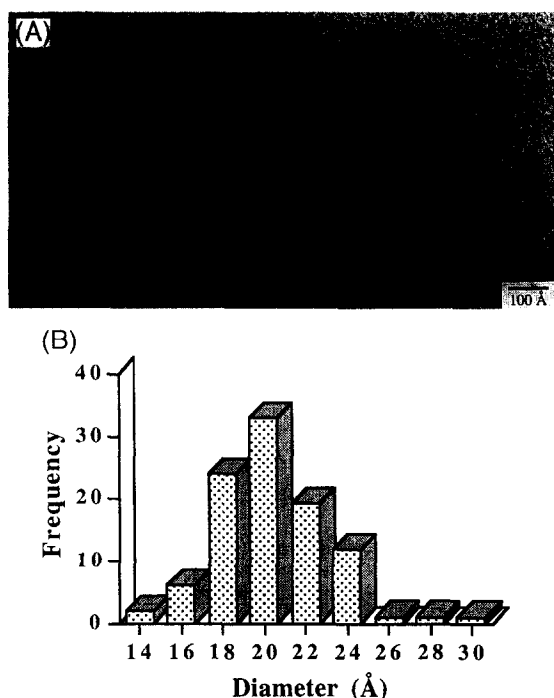

Fig. 2. (A) Transmission electron micrograph of the $Ir_{\sim 190-450}$ nanoclusters generated from the cyclohexene hydrogenation starting with 1.2 mM **1**, 1.65 M cyclohexene and 40 psig H_2 in acetone. The Ir nanoclusters (the dark, roughly spherical ca. 20 Å particles) are well dispersed in the polyoxoanion matrix (the small, granular particles, as demonstrated via independent TEM studies of the polyoxoanion alone, done as a control [6]). The bottom, left-most edge shows the TEM image of the end of the sample and then the carbon-film background. (B) Histogram of the Ir nanocluster diameters. The mean diameter is 20.3 Å, with a standard deviation of 2.8 Å, from a sample population of 366. (Details for the TEM studies are available elsewhere, including a variety of control experiments which demonstrate that the samples examined are TEM-beam stable and are also representative of the rest of the sample [7].)
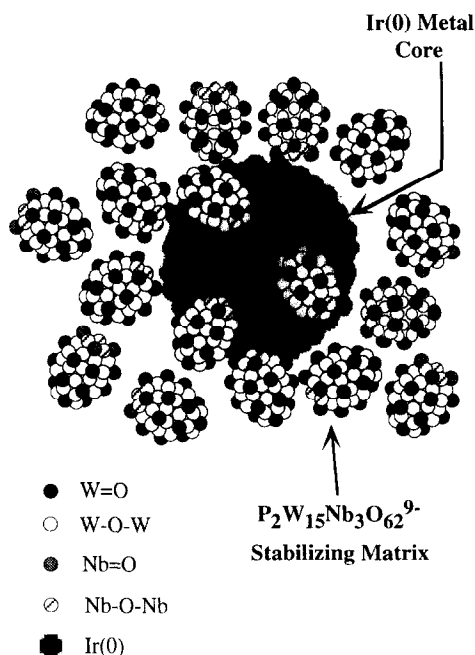
sake of convenience and simplicity, as $Ir(0)_{\sim 300}$, although the reader is urged to remember that this *does not* mean that a single, exactly $Ir(0)_{300}$ nanocluster is present nor implied.) An idealized, roughly-to-scale view of the polyoxoanion- and Bu_4N^+-stabilized $Ir(0)_{\sim 300}$ nanoclusters is provided in Fig. 3. Spectroscopic evidence [6,7] indicates that the $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion has been converted to its well-known [3]b Nb–O–Nb bridged-aggregate form, $P_4W_{30}Nb_6O_{123}^{16-}$, via the reaction $2P_2W_{15}Nb_3O_{62}^{9-} + 2H^+ \rightarrow H_2O + P_4W_{30}Nb_6O_{123}^{16-}$ (the source of the required two H^+ is from hydrogen, $H_2 \rightarrow 2H^+$ and $2e^-$ [6]). However, the polyoxoanion is shown in Fig. 3 as its monomer, $P_2W_{15}Nb_3O_{62}^{9-}$, again for the sake of clarity and simplicity.

2. Important background information: key terms, definitions, and literature

These new nanoclusters are part of a rapidly growing literature reporting more stable, and occasionally isolable, transition metal colloid or nanocluster materials [9–17]. Such new nanoclusters are often prepared, as in the present case, in *organic* solvents rather than in water, the solvent traditionally used for the preparation of colloidal suspensions. They generally carry surface-adsorbed anions, most often of unknown number or even composition, plus R_4N^+ counter ions, the *combination* of which is the key to the nanocluster's stability. The R_4N^+ counter ions can be manipulated to give the nanoclusters solubilities in even organic solvents such as pentane (i.e., for long-chained alkyl groups).

2.1. Key terms and definitions

There are a number of terms and definitions that are crucial to a better understanding of this area and the relevant literature. The literature definitions for several key terms are provided

Three Levels of Ill-Understood
Compositional and Structural Elements
(For Oxide-Supported Heterogeneous
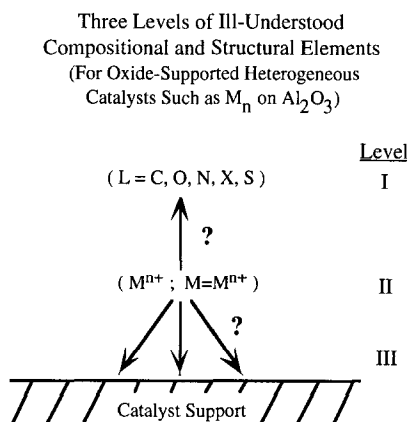Catalysts Such as M_n on Al_2O_3)

Fig. 4. Schematic illustration of the three levels of difficult to establish, and thus poorly understood, compositional and structural elements in solid-oxide-supported heterogeneous catalysts. Level I consists of carbonaceous, oxide, halide or other overlayers; level II shows the uncertainty in the number of metals, their surface and bulk oxidation states, and their degree of coordinative unsaturation (represented as M=M multiple bonds); Level III shows the uncertainty in the almost never directly determined number and type of bonds from the support to the metal.

below, along with appropriate references. Our goal in what follows is to provide a concise, *critical* review of the most recent and important literature in the nanocluster *catalysis* area. Our hope is that such a timely review, if critical (including of our own nanocluster work), will expedite the progress in this promising area in between the borders of classical homogeneous and heterogeneous catalysis.

2.1.1. Nanoclusters (and nanocluster catalysts) vs. traditional colloids (see also footnote 9, p. 8336 elsewhere [6]a)

Compared to nanoclusters [13,14] (1–10 nm, i.e. 10–100 Å) traditional colloids [19] are: typically larger (> 100 Å); of a broader size range; are generally not isolable; are invariably of a completely unspecified molecular composition; typically contain unspecified amounts of surface-adsorbed, catalytic rate-inhibiting [4] [15] X^- (halides), O^{2-}, OH^-, and organic polymer protectants; and typically cannot be reproducibly made (see John Bradley's to-the-point remark on this subject [5]). In addition traditional

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[4] (a) On p. 525 of his review, Bradley [15]a notes that surfactant-stabilized colloidal Pt hydrogenation catalysts are (with italics added to the key part) "... an order of magnitude less reactive than the corresponding supported Pt catalysts, *probably due to the effect the surfactant has on limiting the substrate access to the Pt surface*. A similar effect has also been observed in metal colloid catalysis of olefin hydrogenation in polymerized vesicles [184]". (b) See also the work of others [15]b.

[5] Bradley correctly notes, on p. 490 of his scholarly review [15]a that "perhaps the most important irritant in colloid synthesis is irreproducibility". He goes on to note that we really don't "have any idea on how to control particle size through the proper selection of polymers, solvents, precursors, reducing agents, or metal precursors". He concludes that "the true control of particle size remains the most attractive goal for the synthetic chemist in this field".

G. Schmid, probably the most active researcher to date in nanocluster synthesis and characterization, echoes these points, saying on p. 3 elsewhere [15]c that "the genesis of the formation of distinct large, ligand stabilized clusters is so complex that no reactions can be planned using stoichiometric rules. On the contrary, it is left to chance if larger clusters are formed at all".

Note, then, the significance in this regard of the nanocluster *autocatalytic surface-growth mechanism* [6,7], and its many implications on how to control nanocluster size, detailed in both our initial and subsequent publications [6]b.

colloids often exhibit irreproducible catalytic rates (e.g., of $\geqslant \pm 500\%$) [16], and typically exhibit catalyst deactivation due to particle aggregation plus other unspecified side reactions (e.g., see Fig. 29 in Lewis' 1993 Colloid Catalysis *Chem. Rev.*, [17] where Lewis notes (on p. 2719 for a Pt colloid) that "the platinum-catalyzed system fails due to agglomeration of the platinum colloid"). A non-trivial realization is that many of the above limitations, such as irreproducibility in synthesis, or rates or problems with Cl^- poisoning, closely mirror similar limitations heterogeneous catalysis experts cite for classical oxide-supported heterogeneous catalysts [6] [18]—and for similar reasons. Indeed, for more than a decade we have been using the mnemonic shown in Fig. 4 to emphasize the three levels of hard to establish, and thus generally ill-understood, compositional and structural elements in solid-oxide-supported heterogeneous catalysis.

Because of these severe limitations noted above inherent to *classical* colloids (and classical heterogeneous catalysts!), it has not been possible—despite the long and extensive history of transition metal colloids [19], and their study in catalysis [16,17,19]—to exploit their inherent *potential* as soluble analogs of heterogeneous catalysts. Restated, it has not been possible previously to develop highly reactive, selective and *mechanistically well understood, and thus rationally modifiable*, soluble metal-particle catalysts. (Imagine trying to do a kinetic and mechanistic study, or even to empirically optimize, traditional colloidal catalysts that can't be made reproducibly, can't be isolated, must always be generated in situ, and whose resultant

rates vary by $\geqslant \pm 500\%$!) Note that the molecular formula of virtually every traditional colloid is so poorly known that, even if it *could* be isolated and thus weighed out, one wouldn't be able to calculate the molarity of the resultant catalyst solution since a molecular-formula-derived molecular weight is not available.

2.1.2. Monodispersed nanoclusters

Monodispersity, a term best known from the polymer literature, means, in essence, that one has a single molecule, a single type of chemical entity, or a single chain length in the case of a polymer. In terms of mass (weight) average (M_W) and number average (M_N) molecular weights, monodispersity is defined by $M_W/M_N = 1$.

The simple but important point here, one available only following a careful and thorough reading of the nanocluster [13,14] and colloid [19] literature, is that nanoclusters with $\leqslant 10-15\%$ size dispersions are (mis)designated as 'monodisperse' [7] (a clear misuse of at least the rigorous term). We will, however, designate such nanoclusters as 'near monodisperse', and suggest adoption of this term in the nanocluster literature. The question then arises of "what is the absolute state-of-the-art in terms of preparing 'near monodisperse' nanoclusters"? The record appears to be held by Bell labs and the work of Steigerwald, Brus and co-workers, whose micellar-template produced CdSe and CdS *semiconductor* nanoclusters are within $\pm 5\%$ of being monodisperse, specifically their 48.5 ± 2.5 Å $[(CdSe)_{1800 \pm 250}](SR)_x$ thiolate-capped semiconductor nanoclusters [20]. (Even the past use of HPLC [21]a or gel electrophoresis [21]b to separate clusters into more monodisperse fractions yields ca. $\pm 10\%$ size-variant, 33.9 ± 3.2 Å CdS nanoclusters.) Note, however,

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[6] See Bond's review where he details key remaining problems in heterogeneous catalysis, especially in, ultimately, the lack of atomic level compositional and structural information needed to construct reasonable and reliable mechanisms in heterogeneous catalysts [18], a situation summarized schematically in Fig. 4 of the present contribution. For example, see p. 491 (Cl^- poisoning from the use of MX_n precatalysts, especially for 'RuCl$_3$'; or S^{2-} if SO_4^{2-} is used), or see p. 495 (irreproducibility in syntheses and rates in heterogeneous catalysts).

[7] Bradley has similarly noted this problem in his review [15]a, remarking that the word 'monodisperse' has been used in the literature to describe $\pm 10\%$ size-varied nanoclusters (undoubtedly because $\pm 10\%$ has been the state-of-the-art in synthesizing size-selected nanoclusters). Such size distributions are typically determined by TEM.

that possible transition-metal analogs of such micellar surrounded or RS^- capped nanoclusters would be *poisoned* (non) catalysts, based both on their lack of surface coordinative unsaturation and on literature precedent detailing the effects of such surface poisons (see p. 490 elsewhere [15]a). Also note the analogy here to *CO-poisoned*, and hence catalytically less intresting, $M_x(CO)_y$ 'nanoclusters'.

Another key point is that virtually every review of colloids or nanoclusters cites, as a central problem in nanocluster science, the need to learn how to *reproducibly* synthesize even $\pm 10\%$ nanoclusters *of a prechosen size* [13–15]. A corollary here, one again echoed in the extant literature, is that virtually nothing is known about the *mechanisms* of nanocluster formation [8] [22]. However, our published [6,7] work on the mechanism of formation of polyoxoanion-stabilized $Ir(0)_{\sim 300}$ and $Ir(0)_{\sim 900}$ nanoclusters (plus a paper submitted for publication [6]b)—especially our demonstration of a surface autocatalytic growth mechanism—reveals some of the best available mechanistic insights to date into how to grow near monodisperse nanoclusters of a desired size.

2.1.3. 'Magic number' nanoclusters

Full shell $M(0)_n$ nanoclusters are termed 'magic number' clusters [9] when $y = 13$, 55, 147, 309, 561, 923, 1415,... and are described by the equation $y = 10n^2 + 2$ where $n =$ an integer, $1,2,3,\ldots$, representing the number of
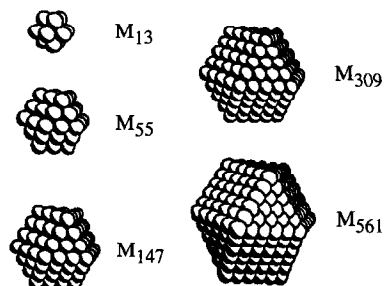

Fig. 5. Idealized representation of hexagonal close-packed (hcp), full-shell clusters, termed 'magic number' clusters in the literature [23] (i.e., they are really just 'full-shell stability' clusters, in which each metal atom has the maximum number of hcp nearest neighbors). Although Ir(0) metal itself is of a somewhat different, cubic close-packed (ccp) structure, the important point is that the number of surface atoms for the *n*th outer shell of atoms is $10n^2 + 2$, for either the above illustrated twinned cubooctahedra structures (with their hcp atoms), *and* for cubooctahedra structures [such as ccp Ir(0)] or icosahedral structures) [23]a,e.

shells packed around a central atom [23] (see Fig. 5 from our earlier publication [6]a). Our attention peaked when we realized that we had prepared Ir(0) nanoclusters *that centered around two of the magic numbers, $Ir(0)_{\sim 300}$ and $Ir(0)_{\sim 900}$*, without trying and even in our first-ever nanocluster syntheses [6]a. The available literature [23] was of no help in giving real insights into *why* magic numbers tended to form, so this has remained a question in the area. However, our mechanistic work has since offered a simple, seemingly compelling explanation for the formation of magic number nanoclusters, and the interested reader is referred to that work [6]b.

2.1.4. Definition of homogeneous vs. heterogeneous catalysts

The following important definition is adapted from our recent nanocluster publication [7]. It employs Schwartz's more modern definitions [24] of 'homogeneous' and 'heterogeneous' catalysts, which replace the classical, solubility-based definitions that equate 'heterogeneous' with 'insoluble', and 'homogeneous' with 'soluble', but which say nothing about the *more important issue* of the homogeneity or heterogeneity of the catalyst's active site(s).

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[8] See also footnote 5 citing Bradley's and Schmid's comments on this topic back.

[9] (a) The term 'magic number' is somewhat misleading and thus controversial. A better term for these clusters would seem to be 'full-shell' clusters, that is clusters which possess some extra stability in part simply due to their close-packed, full-shell nature, a situation where each Ir atom has the maximum number of nearest neighbors. (b) A good discussion of the first real 'magic number clusters' (of a different type) M_n (M = Na, K, Cs; $n = 2$, 8, 20, 40, 58, 92, 138, 196, 260, 344, 440 and 558), plus a good discussion the difference of these magic numbers from those based on icosahedral or cubo-octahedral structures, is available elsewhere [23]b.

Schwartz's definition deals with the active site issue by equating, instead, a homogeneous catalyst as one that has uniformity (homogeneity) in its active sites, while a heterogeneous catalyst is one that has a multitude of (different, heterogeneous) active sites, Fig. 6.

The key, then, is that nanocluster catalysts are really 'soluble *heterogeneous* catalysts' (heterogeneous since they present a $\pm 15\%$ size range of nanoclusters, plus a range of Ir metal surface active sites and, presumably, defects). However, at the limit of true monodispersion (and without adatoms or surface defects) a 4-shell $Ir(0)_{309}$ magic-number cluster with exactly 309 Ir(0) atoms, for example, would be as close as possible to a 'soluble *homogeneous* catalyst', even if different crystal faces are still present. Therefore, a proper nomenclature for our $Ir(0)_{\sim 300}$ · polyoxoanion catalysts is 'soluble heterogeneous catalysts', or 'soluble hybrid heterogeneous–homogeneous catalysts' (or even "soluble 'near-homogeneous' catalysts" if one follows our earlier, 'near-monodisperse' nomenclature).
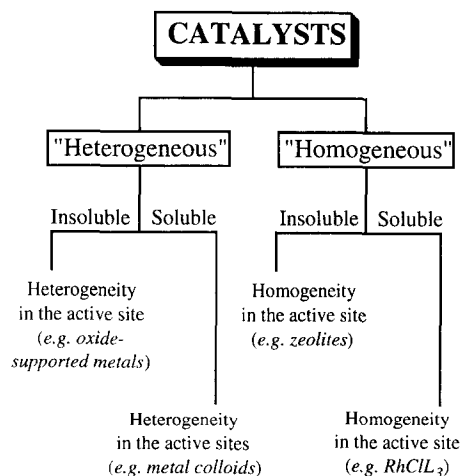
Fig. 6. Revised classification of 'homogeneous' versus 'heterogeneous' catalysts (adapted and expanded following Schwartz's suggestions [24]). This classification scheme emphasizes the (harder to determine) homogeneous versus heterogeneous nature of the active site over the (more easily determined) solubility or insolubility of the catalyst, since the former is more crucial in determining the catalyst's selectivity.
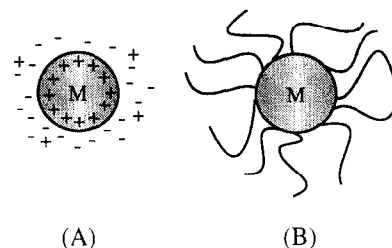
Fig. 7. A schematic illustration for (A) an electrostatically stabilized metal (M) particle (i.e., one stabilized by the adsorption of ions and the resultant electrical double layer), and (B) a sterically stabilized metal particle (i.e., one stabilized by the adsorption of polymer chains).

2.2. Key literature on colloid and nanocluster stabilization: inorganic ('charge') and organic ('steric') stabilization mechanisms

Understanding how traditional colloids are kinetically stablized against aggregation (and thus against the precipitation of bulk metal) is central to understanding what makes nanoclusters or 'nanocolloids' isolable. Historically, colloids and nanoclusters were prepared in aqueous solution in the presence of stabilizing agents, resulting in either so-called 'charge stabilization' (e.g. by the adsorption of ions such as Cl^-), or 'steric stabilization' (e.g. by the surface adsorption of polymers), Fig. 7 [25,26] (adapted from the literature [27]). The surface-adsorbed halides or polymers stabilize colloids kinetically [10] by inhibiting, electrostatically or sterically, respectively, further particle aggregation. A literature example of some relevance to the $Ir(0)_{\sim 300}$ nanoclusters in the present review is the collection of Ir colloidal particles pre-

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[10] It is perhaps worth emphasizing that nanocluster and colloid stabilization is, at least to date, a totally kinetic phenomenon. That this should be the case can be seen by considering the $\Delta H_{vaporization}$ of bulk Ir(0) metal, 159 kcal/mol (see footnote 47 elsewhere [6]a). This in turn means that 12 coordinate Ir(0) in the bulk solid experiences an average bond energy of $159/(12/2) = 26$ kcal/mol (12/2 since it takes 2 Ir atoms to form 1 Ir–Ir bond). This back-of-the-envelope analysis reveals the driving force for $Ir(0)_x$ nanoparticles to aggregate to the thermodynamically favored, low-surface-area solid, thereby regaining the Ir–Ir bonding present in bulk Ir(0).

pared by refluxing a methanol–water solution of Na_2IrCl_6 in the presence of polyvinyl alcohol. As is typical for a traditional, water-prepared and soluble colloid, the *exact composition* of the resulting 17 ± 4 Å nanoparticles *is unknown*, '$[Ir_aH_bO_c(OR)_dCl_e(polyvinyl\ alcohol)_f]^{x\pm}$' (R = Me, H) [28].

A feature of the above literature Fig. 7a that causes confusion is the '+ + +' surface charge shown on the metal particle. Actually, it is *not* a full positive charge, but more of a '$\delta^+\delta^+\delta^+$' that *is an electrostatic charge mirror* produced by the adsorption of X^- anions [29] (typically Cl^- in classical colloids) to the surface of the coordinatively unsaturated, electron-deficient metal surface. The resulting particles are rendered anionic. Thus, similarly charged colloidal particles electrostatically repel other via an anionic, charge-based kinetic stabilization towards aggregation. The counter cations necessary for charge balance, plus more anions, are also present in what is closely analogous to the electrical double-layer at an electrode surface [29]b, Fig. 7A.

Note that such a charge-stabilization picture is fortified experimentally for the $Ir(0)_{\sim 300}$ nanoclusters by our published demonstration, using both electrophoresis and ion-exchange resins, that these nanoclusters are indeed anionic due *only* to the polyoxoanions adsorbed/bonded to their surface [6]a—one of the few direct demonstrations in the literature of a nanocluster's surface charge. Significant here is that we also ruled out the presence of a reduced iridium, anionic core '$Ir^{n-}_{\sim 300}$' nanocluster by the use of careful H_2 reducing agent stoichiometry studies; also ruled out were the presence of surface hydrides, 'H^-'. Both of these demonstrations are nearly unheard of in either the transition metal colloid or nanocluster literature.

Two recent literature reports support the above polyoxoanion charge-stabilization picture. Anson and co-workers have reported that even low-basicity, classical polyoxoanions such as $P_2W_{17}CrO_{61}^{7-}$ show 'unusually strong adsorption' to a Hg electrode surface [30]a. In addi-

tion, Klemperer, Gewirth and co-workers have reported that α-dodecatungstosilicate, α-$SiW_{12}O_{40}^{4-}$, self-assembles and becomes 'strongly bound to (a) Ag(111) surface' under acidic conditions [30]b.

Apparently, because they have not done crucial experiments like electrophoresis to demonstrate the charge on their nanoclusters, a recent paper implies that their long chain R_4N^+ cations are simply adsorbed directly onto a putative anionically charged nanocluster (see Fig. 4 on p. 363 elsewhere [31]). Unfortunately, the charge on a colloid or nanocluster particle is *rarely* demonstrated experimentally, and was not demonstrated in the paper in question. Moreover, the elemental analyses provided in the paper show the presence of Cl^-, Br^- or other anions in every case [31]; hence, there is no reason to think that the R_4N^+ are adsorbed directly to a little precedented 'reduced metal surface' as written, but rather that the *anions present* (Cl^-, Br^- or OAc^-) are adsorbed directly to the metal surface.

The confusion in Figs. 3 and 4 elsewhere [31] appears to have mislead authors of a 1994 *Science* paper on Pd nanoclusters [9]h. In this otherwise elegant, combined TEM/STM study, the authors appear to be confused about the
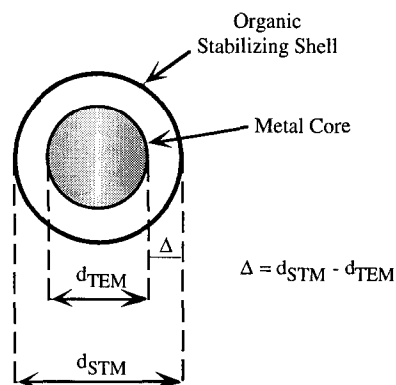

Fig. 8. Distances measured by TEM and STM microscopies (adapted from Reetz and co-workers [32]). Note, however, the ambiguity about where the inorganic anion (Cl^-, or other X^-) fit into this picture.

charge on their nanoclusters, in part because they have not determined it experimentally (e.g., by electrophoresis). In this *Science* paper [9]h, the stabilizing R_4N^+ (and Br^-, vide infra) surface layer on 40 Å Pt nanoclusters was visualized directly by comparing TEM ca. metal core diameter (d_{TEM}) and STM ca. total particle diameter (d_{STM}) image distances, Fig. 8. These authors' intriguing results are that the $\Delta(d_{STM} - d_{TEM})$ distance difference increases, as expected, as the R_4N^+ chain length grows: $(C_4H_9)_4N^+$ $(d_{TEM} = 3.4$ Å, $d_{STM} = 4.7$ Å; $\Delta = $ **1.3 Å**); $(C_8H_{17})_4N^+$ $(d_{TEM} = 4.1$ Å, $d_{STM} = 6.9$ Å; $\Delta = $ **2.8 Å**); $(C_{18}H_{37})_4N^+$ $(d_{TEM} = 4.0$ Å, $d_{STM} = 8.4$ Å; $\Delta = $ **4.4 Å**). However, this paper [11] ascribes the larger d_{STM} vs. the d_{TEM} distances *solely* to the R_4N^+, and ignores the Br^- that is known to be present by elemental analysis [32]a. A simple test for the anion's stabilizing influence, in such X^- equals halide cases, is to survey the relative stabilities (and catalytic activities) of the $R_4N^+X^-$ series. The expected decrease in nanocluster stability is $Cl^- > Br^- > I^- \gg F^-$ for the same reasons that electrochemists know that "F^- solutions in contact with Hg are the standard systems for checking the theory of *nonspecific adsorption*" (italics have been added) to electrode surfaces [30]c.

It now becomes at least partially apparent why polyoxo *polyanions* plus their associated *multiple* R_4N^+ are excellent at stabilizing our $Ir(0)_{\sim 300}$ 'nano-colloidal' particles. As we stated previously [6]a: "The stabilization of the poly-

oxoanion is of a little precedented type [12] [33], one *apparently* due to the *combined high charge* [13] [34] plus *significant steric bulk* present *intrinsically* within the *poly*anion and *poly* Bu_4N^+ cation components" of [14] $P_2W_{15}Nb_3O_{62}^{9-}$ and its associated Bu_4N^+ and Na^+. Key features of this unusual type and strength of nanocluster stabilization appear to be: (i) the basic $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion, with its chelating 6 basic surface oxygens [and its even larger, but slightly less basic, Nb–O–Nb anhydride form, $\{(P_2W_{15}Nb_3O_{61})_2-O\}^{16-}$] [6]a[7]; (ii) the large size of the polyoxoanion and its associated, multiple R_4N^+ and Na^+; (iii) the lack of competing, surface-adsorbed O^{2-}, OH^-, Cl^-, or other *mono*anions (i.e., the

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[11] In an even more recent paper [32]b, the thickness of what is shown (see Fig. 2 elsewhere [32]b) as an 'R_3N:' protective layer (but that is almost surely, instead, a R_3NH^+ stabilizer) was derived in *solution* from a measurement of the hydrodynamic Stokes' radius. In this case, the stabilizing layer diameter was much smaller than expected, a result attributed to 'folding' of the alkyl groups over the surface of the metal cluster rather than full extension of the alkyl chain (as examined by ^{13}C NMR measurements). Again, it's likely that anions (probably Cl^- in this case [32]b) are the only species directly coordinated to the metal's surface in this system.

[12] (a) The apparent keys to the high stabilizing effect of the $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanions are: (i) the combined effects of 6 highly basic and chelating Nb–O⁻ and Nb–O–Nb oxygens; (ii) the fact that the 3^- surface-charge is localized largely on the (presumably nanocluster-binding) '$Nb_3O_9^{3-}$' end of the $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion; (iii) the fact that the true *surface charge* of the polyoxoanion is *only* 3^- (this prevents unnecessary compacting of the electrical multi-layer [34]), *plus* the fact that the rest of this special type of custom-made polyoxoanion is *both* very large (ca. 12×15 Å) *and* has relatively little surface charge density. (The lack of anionic surface charge density in the rest of the polyoxoanion, i.e., past the formal 3^- '$Nb_3O_9^{3-}$' component, can be seen by rewriting the polyoxoanion as it actually exists structurally, i.e., $P_2W_{15}Nb_3O_{62}^{9-} \equiv [(PO_4^{3-})_2(W_{15}O_{45})^0(Nb_3O_9)^{3-}]^{9-}$. Note the *formal* lack of surface anionic charge density on the $(W_{15}O_{45})^0$ part of the polyoxoanion.)

[13] (a) High charge density and high ionic strength within the colloid-stabilizing mulitlayer reduces its thickness, which in turn gives rise to *less* stable particles, at least in classical, H_2O soluble colloids [19,34]. (b) Although the thickness of the multilayer necessarily increases with higher charge polyoxoanions and their associated larger number of accompanying R_4N^+ counter cations, a competing *inverse* dependence upon the *charge* (at least in classical H_2O soluble colloids) is the case [34]. The needed, obvious fundamental nanocluster stability studies are in progress (i.e., probing the role of different R_4N^+, different size and charge polyoxoanions, and different types and polarity solvents).

[14] Note that, rigorously speaking and as discussed in greater detail elsewhere [6a,7], ultracentrifugation MW experiments indicate that the polyoxoanion is largely present as its Nb–O–Nb anhydride form, $(Bu_4N^+)_{10}(Na)_6[(P_2W_{15}Nb_3O_{61})_2-O]$. Control experiments are in progress to detect the difference, if any, in the nanocluster stabilizing abilities and catalytic activity of $Ir(0)_{\sim 300}$ stabilised by this anhydride form vs. the related monomeric form, $(Bu_4N^+)_6(Na)_3[P_2W_{15}Nb_3O_{62}]$.

$Ir(0)_{\sim 300}$ surface is relatively clean, *coordinatively unsaturated*, and thus *available* for association with the polyoxoanion; and (iv) the high charge/induced dipole, *charge-mirror effect* [29] induced by the highly charged polyoxoanion. This is not to say that we are even close to fully understanding the *apparently* special nature [15] of polyoxoanion-based nanocluster stabilization. [16] Indeed, in our first publication we also noted that "further studies of other polyanions with other R_4N^+ counter cations will be needed ... to better understand this unusual stabilization mode". Hence, these and other fundamental studies are a key component of work in progress. One advantage of our ca. 12×15 Å $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion is that it is large enough to be directly and individually visualized by HR-TEM (actually, they are easily seen even in low-resolution TEM, *and do cluster around the Ir$_{\sim 300}$*; see Fig. 8a elsewhere [6]a). Hence, HR-TEM, STM and additional characterization studies of $Ir(0)_{\sim 300} \cdot$ polyoxoanion nanoclusters are goals of work in progress.

Noteworthy within this context is that the nanocluster stabilization provided by the polyoxoanion and the Bu_4N^+ counter cations in $Ir(0)_{\sim 300} \cdot$ polyoxoanion is apparently very special in a second and perhaps even more significant way—it provides the nanoclusters with sufficient stabilization to allow their isolation, yet it also affords the *isolated* $Ir(0)_{\sim 300}$ a surface accessibility and thus a very high catalytic reactivity (vide infra).

One may wonder how the discovery of $Ir(0)_{\sim 300} \cdot$ polyoxoanion nanocluster catalysts was made—was it 'accidental'? Although the discovery was by no means completely 'by design', assurance of the most important property of catalytic activity and long lifetime was no accident. It was, instead, the result of some old-fashioned, "Mittasch-type" [17], catalyst survey experiments, begun in 1982, in which each of the following was varied and at least partially optimized: the transition metal and organometallic complex, the polyoxoanions ($SiW_9M_3O_{40}^{7-}$, $P_2W_{15}V_3O_{62}^{9-}$, $M(V) = V$, Nb, others), and the solvent [8]a. These survey experiments demonstrated that the $(1,5\text{-COD})M \cdot P_2W_{15}Nb_3O_{62}^{8-}$ (M = Ir, Rh) precatalysts in acetone or EtOH provided *high rate, long-lived* hydrogenation catalysts. Hence, and from that point on, we were assured of discovering an active and relatively long lasting catalyst, one that would also probably have a novel composition. This latter point follows from the fact that the $(1,5\text{-COD})M \cdot P_2W_{15}Nb_3O_{62}^{8-}$ precatalysts were without precedent (i.e., as either compositions of matter or as catalyst precursors), and since early control experiments proved that only custom-made, *basic* polyoxoanions such as $P_2W_{15}Nb_3O_{62}^{9-}$ or $SiW_9Nb_3O_{40}^{7-}$ (but not the non-basic $P_2W_{18}O_{62}^{6-}$, for example [8]c) avoided the formation of bulk Ir(0) *and* gave the highest catalytic rates. The 'only' but significant problem that remained was "what is the actual catalyst"?

A two-student effort followed, beginning in 1986 and ending 8 years later with Dr. Yin Lin's Ph.D. thesis in 1994 [6,7]. During this time we developed and published a more direct and more general solution to the classic, often

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[15] The large $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion size, combined with a specific, highly basic, and 6 oxygen chelating nanocluster binding site, *plus* the lack of anionic charge density in the rest of the polyoxoanion, is a range of features that would *seem* to be unlikely to be matched easily in other systems. The intriguing concept that comes to mind here is that the $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion may be a special type of 'giant citrate trianion' (citrate^{3-} is one of the oldest and best stabilizers of, for instance, classical gold colloids).

[16] An interesting analogy is apparent between polyoxoanion-oxide-stabilized metal particle catalysts and solid-oxide-immobilized heterogeneous metal particle catalysts: *in both cases, the oxides prevent particle agglomeration or sintering*, one in solution, the other in the solid state.

[17] A. Mittasch, in 1909, is generally credited for the strategy of extensive catalyst screening to invent new catalysts compositions. Specifically, his ca. 6500 screenings of ca. 2500 catalysts led to the still largely unchanged industrial NH_3 synthesis catalyst (see reference 1 and the discussion of this provided by Ertl elsewhere [50]d). It is a non-trivial observation that this strategy is still important today in catalysis, not to mention 'modern' strategies of drug discovery such as combinatorial synthesis.

perplexing mechanistic problem, "Is it a homogeneous or a heterogeneous catalyst?" [7]. Solving this problem was considerably harder due to the inherent hybrid, homogeneous–heterogeneous nature of the Ir(0) $_{\sim 300}$ catalyst, but in the end we invented a more general and robust paradigm for solving this question, in part due to the fact that our method had been both intrinsically developed and tested on a previously unknown, hybrid, homogeneous–heterogeneous catalyst, Ir(0) $_{\sim 300}$. Once we solved this mechanistic problem, we were rewarded with the discovery of a novel, polyoxoanion-stabilized Ir(0) $_{\sim 300}$ nanocluster catalyst [7]. The discovery of the Ir(0) $_{\sim 300}$ · polyoxoanion nanoclusters was, then, partially serendipitous, but also the direct result of a catalyst development paradigm involving a *near-simultaneous* combination of synthesis, characterization, catalytic testing and mechanistic studies (see Fig. 3 elsewhere [4]f) over a period of 14 years.

2.3. Prior catalytic studies of nanocluster hybrid heterogeneous–homogeneous catalysts

The first example of a true, proven, non-polymer-protected nanocluster catalysis is the already classic Moiseev and coworkers' work on giant Pd $_{\sim 570}$ nanoclusters of approximate composition [Pd $_{\sim 570 \pm 30}$ (phen)$_{63 + 3}$ (OAc)$_{190 \pm 10}$]$^{x-}$ (the overall charge, x^-, and the associated counter cations are unknown, however, even though a neutral complex and the implied cationic 'Pd$_{570}$$^{180+}$' are written; surface Cl$^-$, OH$^-$ and O^{2-} are also probably present, [9]g, [35]). These nanoclusters were shown to catalyze ethylene and propene oxidation (Wacker chemistry); alcohol oxidation; olefin hydrogenations, isomerizations, and dimerizations [35]a; and, more recently, oxidative phenol carbonylation [35]c. Their catalytic reproducibility was demonstrated to be ca. ± 10%, the first such demonstration, an important point that appears to be little known since it is buried without emphasis inside this lengthy paper. *Previously, it was believed that only*

single metal homogeneous catalysts could have a kinetic reproducibility of ⩽ 15%! (see page 4894 and footnote 28 elsewhere [7]). This myth is dispelled by the Moiseev and coworkers' work, and also by our demonstration of a ± 10% kinetic reproducibility for our Ir(0) $_{\sim 300}$ nanoclusters [6,7]. The Pd $_{\sim 570}$ nanoclusters are isolable and can be redissolved, with only 10–30% of their activity being lost during their isolation [35]a. Unfortunately, however, these authors make no comparison of their Pd $_{\sim 570}$ nanocluster catalyst to a traditional, solid-oxide-supported heterogeneous Pd catalyst (i.e., to determine which catalyst is the most reactive on a per-active-Pd basis).

There are very few other examples of catalysis by non-polymer-coated nanocluster size particles. Most notable are two important papers by Reetz and collaborators [9]h, [32]a–i. This work is unparalleled in several respects: (i) its electrochemical method of synthesis under argon of, for example, a [(octyl)$_4$N$^+$]$_b$[(Pd$_a$Br$_b$)$^{b-}$] nanocluster is as simple, as versatile [e.g., to other (R$_4$N$^+$)$_n$ (Y^{n-}) electrolytes as nanocluster stabilizing agents], and as high yield (> 95%) as any reported synthesis—it promises to be a major synthetic advance in the area; (ii) its nanocluster isolation procedure is impressively simple (i.e., the ones made so far just precipitate from solution); and (iii) the procedure offers size control by adjusting the current density (higher current densities give greater nucleation rates and thus smaller nanoclusters; electrochemical precedent and equations are even available to help semi-quantitatively guide the syntheses [32]a). This work also boasts an all-elements elemental analysis (adding to 99.7%). This little precedented situation allows the authors to conclude that an oxide coating, 'PdO', is not formed (i.e., the nanoclusters are reported to be stable to air)—although the author's more recent EXAFS data on a related Pt/Pd nanocluster indicates O^{2-} on its Pd surface (and in its Pt core!) at levels of 7–30% by weight of O$_2$ (estimated by difference from their Table 1 analytical data) [32]f. Professor Reetz's very

recent paper unequivocally demonstrates that Co, Fe or Ni nanoclusters are indeed air sensitive, forming (in the case of Co) the oxide, $(CoO)_n$ and maybe $(Co_2O_3)_n$ [32]j. The available data leads us to suspect that many literature nanoclusters may contain an oxidized layer (see also Reetz's comment in footnote 12 elsewhere [32]c). We emphasize, however, that our own $Ir(0)_{\sim 300}$ nanoclusters do *not* contain O as they have never been exposed to O_2.

In addition, and although not discussed [9]h, [32]a, the observed current yield of $> 95\%$ for $Pd^{2+} + 2e^- \rightarrow Pd(0)$ allows the key conclusion that a reduced, intrinsically anionic '$Pd(0)_x^{n-}$' is *not* formed. This in turn offers virtual proof that the Br^- anions present by elemental analysis are directly coordinated ('specifically adsorbed' [30]c) to the Pd nanocluster's surface. The only problem in this unparalleled work is that the authors ascribe the stability of the nanoclusters to the R_4N^+ [32]a, and again [9]h omit the effect of the Br^- [18].

A series of papers by Bönnemann and coworkers describes R_4N^+ and X^- (X = Cl, Br, OAc) stabilized nanoclusters [11]b, noteworthy because of their isolability. For example, the reduction of PdX_2 (X = Cl, Br, OAc) with $R_4N^+BR_3H^-$ provides 18–40 Å $Pd(0)_n$ clusters of unreported exact composition, $[Pd(0)_nBr_aCl_bH_cO_d(OH)_eB_f]^{x-}[R_4N^+]_x$, although elemental analysis shows ca. 83% Pd and 5–6% Cl or Br. (Although not reported for the present example, a boron analysis of BR_3H^- reduced $Pd(CN)_2$ shows the presence of 1.38% boron in the $Pd(0)_n$ nanoclusters). The resultant $Pd(0)_n$ nanoclusters are *not* stable enough to

support cyclohexene hydrogenation in THF at 25°C without Pd(0) metal formation, which "occurs after 6–7 minutes" (see p. 162 elsewhere [11]b). If, however, these $Pd(0)_n$ nanoclusters are *supported* on carbon, then up to 96,000 total turnovers were demonstrated for the $(octyl)_4N^+$ system, with ca. 10% of the catalysts' activity remaining after the 96,000 turnovers (see p. 166 elsewhere [11]b). The reported activities are claimed as better than that of 5% Pd/C catalysts, although the reported turnover numbers are uncorrected for the number of active Pd, so it is unclear whether the true, per-Pd activity is actually higher, the same within experimental error, or lower.

Of particular interest to the present review is Bönnemann and coworkers' report of the preparation of ca. 1.5 nm [11]a Ir nanoclusters by a $N(Octyl)_4^+BEt_3H^-$ reduction of 'anhydrous $IrCl_3$' in THF and, at least initially, under an inert, O_2-free atmosphere (but which then were, unfortunately, worked up in air). The resultant red-black, ~ 15 Å Ir nanoclusters are reported as very soluble in organic solvents such as THF or acetone, and can be formulated as '$[N(Octyl)_4^+]_x[\{Ir_aH_bO_c(OH)_dCl_eB_f\}^{x-}]$' {65.5% Ir; 0.27% N; 3.49% H; 19.97% C (%B, %Cl, %O not reported)} [11]b. The solubility and stability of these clusters is again attributed to the presence of $N(Octyl)_4^+$ surrounding the Ir nanoclusters [11]a, although the literature cited previously confirms that a major source of the stability of these nanoclusters is derived almost surely from the presence of surface-adsorbed anionic ligands, which in turn requires the presence of associated, also nanocluster stabilizing, $N(Octyl)_4^+$ counter cations. An advantage of Bönnemann's Ir_n nanoclusters (e.g., compared to our own $Ir(0)_{\sim 300} \cdot$ polyoxoanion nanoclusters) is their more ready synthesis on a several-hundred milligram scale (and on a 2–3 gram scale for Pd, Pt) from commercially available reagents. However, the required reagents are somewhat expensive, and a crucial reagent underpinning the synthesis, 'anhydrous $IrCl_3$', is an ill-defined, insoluble, variable color (blue-

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[18] Another way to realized the importance of the anion that is present (Br^- in this specific case) is to consider the limit of a discrete, coordinatively unsaturated, single metal $Pd(0)L_x$ ($x \leqslant 3$) complex. No organometallic chemist would expect $Pd(0)L_x$ to bind R_4N^+ preferentially vs. the much more basic X^-. For this same reason, a coordinatively unsaturated $Pd(0)_x$ or other $M(0)_x$ nanocluster will bind *basic anions*, exactly analogous to why electrode surfaces are well established to 'specifically adsorb' halide and other X^- or neutral, but basic, ligands [30]c.

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green to red or even black!) material that is, therefore, sold on a %Ir basis only. We believe that the problems with 'anhydrous $IrCl_3$' are the reason we were unable to repeat completely the reported [11]b synthesis [19].

There is also an extensive, older literature of catalytic studies of interesting, but composition-ally ill-defined and typically polymer-protected (i.e., rate inhibited), 'nanocolloids'. Lewis' 1993 review is available for this related—*but concep-tually and distinctly different*—area of the vari-able rate catalysis by non-isolable, and thus irreproducible, [20] polymer-protected classical colloids and nanocolloids [17]. There is other work in this area as well, including interesting work on Ru and Pd nanocolloids [36], important studies from Lewis at GE on colloidal hydrosi-lylation catalysis [37], and a number of other studies of catalysis by colloids [17,38]. There are also extensive studies in the somewhat re-lated area of precatalysts generated by the depo-sition of carbonyl clusters deposited on solid oxides [39]. Note that the traditional, isolable,

and often elegantly structurally characterized $M_x(CO)_y$ complexes of the 'cluster catalysis hypothesis' popularized by Muttertries [40] are generally *not* catalytically active (other than for CO reactions [41,42]), since they are CO poi-soned [21]), and hence are not considered herein as nanocatalysts. [22] In one sense, then, the best nanocluster catalysts summarized in this review can be viewed as the long-sought solution to the 20-year-old 'cluster catalysis hypothesis' [40].

Overall, a careful reading of the nanocluster catalysis literature reveals an important insight: other than the classic work on $Pd_{\sim 570}$ already discussed, there is no other catalytic, kinetic and mechanistic study of a *compositionally well-de-fined*, isolable, and thus $\leq \pm 15\%$ *reproducible* reactivity, soluble *nanocluster catalyst* (and even the compositional characterization of the $Pd_{\sim 570}$ catalysts is less than ideal). Of course, the whole area of *organic solvent soluble* nan-oclusters is a relatively new one [23] [13,14]. The bottom line, then, is clear—in its infancy is *modern nanocluster catalysis*: the rational de-

[19] We attempted to reproduce the synthesis of $(octyl)_4N^+$-stabi-lized 15 Å Ir nanoclusters described elsewhere [11]b for a direct comparison of the catalytic rates to our own $Ir(0)_{\sim 300}$ nanoclus-ters. Unfortunately, and at least in our hands, but under *exactly* the reported conditions (e.g., 1.84 g anhydrous $IrCl_3$, titrated $(octyl)_4N[B(ethyl)_3H$, 16 h reflux under argon, workup under air), the synthesis gave a low, 80 mg yield of a black, waxy material (vs. the reported 360 mg of a grey, dry powder) due to the failure of much of the $IrCl_3$ to dissolve (the waxyness is due, presumably and in turn, to the presence of the excess $(octyl)_4N^+$ that is present since all the '$IrCl_3$' [52] didn't react). TEM did confirm that our 80 mg of product contains the reported [11]b ca. 15 Å iridium nanoclusters. However, we have not yet suceeded in using the waxy product to obtain the desired reliable, quantitative catalytic rate (for comparison to our $Ir(0)_{\sim 300}$ rates), due to problems in qunatitatively manipulating such small amouts of a waxy material.

[20] A good example here is the catalysis of hydrosilylation by Pt complexes, now known from Lewis' work to be due to $Pt(0)_n$ colloid catalysis. It is especially interesting that Pt catalyzed hydrosilylation is an area notorious for its irreproducibility *and for the importance of trace O_2 to keep the catalyst active and, apparently, highly dispersed* (see footnote 11 elsewhere [37]d). An initial study of O_2 plus Pt colloids is available [37]e. It is furthermore very interesting to note that supported Pt redisperses to smaller particles under O_2 at 823 K [37]f.

[21] This suggests to us that it may, however, be possible to photolytically dissociate CO ligands from well-characterized $M_x(CO)_y$ in the presence of polyoxoanions or other nanocluster stabilizing ligands such as $(R_4N^-)_3[citrate^{3-}]$ and, for example, cyclohexene plus a H_2 flush (to remove the CO). We are not aware of experimental scrutiny of such potentially promising synthetic routes to nanoclusters, and hence urge some interested group to explore them.
Professor K. Suslick and co-workers have demonstrated that mononuclear metal carbonyls, $M(CO)_x$, yield nanostructured ma-terials when *sonicated* using a high-intensity ultrasound probe [40]e.

[22] A most interesting insight in this regard is that Mutterties' $CO + H_2$ reaction using $Ir_4(CO)_{12}$ as precatalyst, and in $NaCl/AlCl_3$ molten salt, might be correctly viewed as a $AlCl_4^-$ stabilized Ir_4 nanocluster reaction [42]. *If* a correct view (i.e., if species such as mononuclear $HIr(CO)_4$ are not the true catalysts, and *if* nanoclusters can in general survive such conditions), then this insight may foretell a little investigated area of nanocluster catalysis in molten salt media.

[23] Indeed, when we began these studies ca. 1.5 decades ago, organic solvent-soluble 'colloids' were virtually unheard of, and it was generally believed that they would be unstable. Obviously, this is another reason that catalysis by well-defined nanoclusters is an undeveloped area—the required catalyst materials simply did not exist until more recently.

velopment of 'hybrid heterogeneous–homogeneous' nanocluster catalysts that are based on reproducible syntheses, are compositionally and structurally well-defined, and which exhibit homogeneous catalysis-like ±15% reproducible rates, high activity, and long lifetimes, even in solution and eventually at temperatures ⩾ 100–200°C. Perhaps most exciting from our point of view will be the detailed kinetic, mechanistic and spectroscopic studies of such modern nanocluster catalysts, efforts which promise to help provide the understanding that should eventually lead to more rational catalyst design for all types of metal particle catalysts.

3. Review of Ir(0)$_{\sim 300}$ · polyoxoanion-stabilized nanoclusters

In what follows we briefly summarize the data to date on polyoxoanion-stabilized Ir(0)$_{\sim 300}$ nanoclusters, specifically: (i) their synthesis, (ii) their compositional and structural characterization; and (iii) their catalytic activity and lifetime in the prototype structure-insensitive reaction [43] catalytic olefin hydrogenation (chosen for initial study because of its well-studied nature [44]). Our work includes a comparison of the catalytic rates and lifetimes of Ir(0)$_{\sim 300}$ to traditional, solid-oxide-supported heterogeneous catalysts, such as Exxon's well characterized 80% dispersed 1% Ir(0) on η-Al$_2$O$_3$ [45]. Also reviewed for the Ir(0)$_{\sim 300}$ nanoclusters are (iv) their stability above room temperature; and (v) their two-electron reduction of the polyoxoanion support by H$_2$, a soluble-oxide form of 'hydrogen spillover'. This latter observation is important as a conceptual link between such soluble nanocluster and traditional, solid-oxide-supported heterogeneous catalysts.

3.1. Synthesis

The precatalyst [(n-C$_4$H$_9$)$_4$N]$_5$Na$_3$[(1,5-cyclooctadiene)Ir · P$_2$W$_{15}$Nb$_3$O$_{62}$], 1, is the key

to the synthesis of Ir(0)$_{\sim 300}$, one of the reasons this complex has been the target of several Ph.D. theses and multiple years of effort [3,4]. A fully experimentally checked *Inorganic Syntheses* procedure is available, and even this has now been improved upon by a 2 step (30% in time) shorter procedure that provides 60% more of the required polyoxoanion, [(n-C$_4$H$_9$)$_4$N]$_9$[P$_2$W$_{15}$Nb$_3$O$_{62}$], on a 116 g scale [4]e.

The conversion of 1 to the Ir(0)$_{\sim 300}$ · polyoxoanion nanoclusters is the simple reaction of 1 in acetone and under 40 psig H$_2$ with cyclohexene. The desired product is readily isolated by simple precipitation or evacuation [the Ir(0)$_{\sim 300}$ becomes insoluble as the solution becomes less polar due to the 0.5 ml of cyclohexene (in 2.5 ml acetone) being hydrogenated to ca. 0.5 ml of the less polar cyclohexane; centrifugation or filtration can also be used to quickly isolate a lower yield of product] [7]. This synthesis is advantageous in that: (i) it begins with the discrete and very well-defined precursor, 1, [4]a–h (which does, however, still require a couple of weeks to prepare); (ii) the nanocluster-forming step involves only H$_2$, (iii) isolation involves a simple precipitation step, and (iv) the synthesis has proved completely reproducible in at least our hands (4 different co-workers) and under the specified conditions [6]a, [7]. The main *disadvantage* of at least our original synthesis is its small scale, 20 mg 1, which yields only 3 mg (albeit ca. 60% based on Ir) of Ir(0)$_{\sim 300}$ · polyoxoanion. The Ir(0)$_{\sim 900}$ · polyoxoanion is synthesized similarly, but on a larger scale (1.0 g of 1) and in the *absence of cyclohexene*. The resultant Ir(0)$_{\sim 900}$ nanoclusters are isolated in 70% based on Ir (120 mg) by the slow addition of the less polar cyclohexane to the acetone solution. The obvious, needed scale-up experiments and conceivable *in-situ* syntheses (i.e., without the necessity of isolating 1) of both Ir(0)$_{\sim 300}$ and Ir(0)$_{\sim 900}$ are under way, as are studies of why the presence or absence of cyclohexene gives Ir(0)$_{\sim 300}$ or the larger Ir(0)$_{\sim 900}$, respectively.

3.2. Compositional and structural characterization

The review of the literature provided herein reveals that the level of compositional characterization of our catalytic nanoclusters is second to none in the literature—only Reetz's previously mentioned $Pd(0)_x$ nanoclusters are as well compositionally characterized. Specifically, our nanoclusters are the only examples, *of catalytically active nanoclusters*, where the full molecular formula is known, $\{Ir(0)_{\sim 300}[[(P_2W_{15}Nb_3O_{61})_2-O]_2]_{33}\}(Bu_4N)_{\sim 300}Na_{\sim 233}$, including the electrophoretically demonstrated overall (negative) charge, the cation composition, and the absence of surface O^{2-}, OH^-, H_2O, or halide (the latter were all excluded during the carefully controlled, air- and water-free synthesis). Also demonstrated is the source of the nanocluster's negative charge [6]a, namely the coordination of the $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion to the $Ir(0)_{\sim 300}$ metal core [6]a. The isolability and TEM-demonstrated non-aggregation (even after isolation and then redissolving the nanoclusters) are as good as—if not better than—that reported for any other nanocluster catalyst material. The net structural characterization is limited to electron diffraction (proving that the nanocluster's core is identical to authentic $Ir(0)_n$), TEM studies, and unpublished HR-TEM images (which confirm the 20 Å size and crystalline nature of the $Ir(0)_{\sim 300}$ core). There are, we note, better—indeed, elegantly—structurally characterized nanocluster systems in the literature. [24]

3.3. Turnover numbers, catalyst lifetime, and comparison to other Ir(0) heterogeneous and nanocluster catalysts

The turnover numbers (TONs) [46] and lifetimes for the various $Ir(0)_n$ catalysts are summarized in Table 1 [7]. Both the commercial 7.9% dispersed 1% Ir/γ-Al_2O_3 and the low surface area, bulk/precipitated $[Ir(0)_n]$ showed a TON of ca. 3900/h under our experimental conditions (entries 1 and 2, Table 1). Interestingly, the more highly (80%) dispersed 1% Ir/η-Al_2O_3 was not quite as reactive, TON = 1740/h, although the differences are perhaps not rigorously different statistically (i.e., given the error limits cited). The catalyst lifetimes under our conditions demonstrate primarily that the catalysts are indeed active for at least tens of thousands of turnovers, and that the low (7.9%) dispersion $Ir(0)/\gamma$-Al_2O_3 catalyst is, as expected, the most robust and exhibits the highest number of demonstrated turnovers (410,000).

Of special interest is the demonstration that the $Ir(0)_{\sim 300}$ · polyoxoanion nanocluster catalyst gave the same TON per active $Ir(0)$ atom within experimental error (TON = ca. 3200). This is the only such direct comparison in the nanocluster literature, to our knowledge. The $Ir_{\sim 300}$ · polyoxoanion catalyst is also without equal in that it shows a relatively long lifetime of 18,000 total turnovers over 10 days *in solution*, after which it is completely deactivated [7]. (A control experiment confirmed that the $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion alone has no catalytic activity, Table 1, last entry.)

Professor Schmid has also noted this unusual property of our nanoclusters by stating that [9]k "a special reaction has been described where clusters in solution worked as catalysts without recognizable decomposition". Note that, actually, recognizable decomposition *is* present [i.e., our published observation [7] that the catalyst is deactivated after 18,000 turnovers (spanning a period of 10 days), Table 1]. (It is our fault, however, that these points are not apparent to others, as they are buried in a lengthy mechanistic paper [7], one reason we felt that the present review was needed.) In addition, work initially

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[24] Nanoclusters structurally characterized at a state-of-the-art level include, for example, Schmid's $Au_{55}(PPh_3)_{12}Cl_6$ clusters [9]j, the Moiseev and co-workers palladium clusters [35], Bradley and co-workers' thorough NMR studies of CO on palladium crystallites [10]h or ligand-dependent Pt nanocluster structures [10]j, and some impressively characterized RS-stabilized Au nanoclusters [10]k.

Table 1

Comparison of heterogeneous $Ir(0)_n$ catalysts versus polyoxoanion-supported $Ir(0)_{\sim 300}$ catalysts [a]

Catalyst	TON (mol product · mol exposed Ir(0) catalyst^{-1} · h^{-1})	Total turnovers (observed)
Exxon's 80% dispersed Ir/η-Al$_2$O$_3$	1740 ± 250 [b,c]	20,000 [b,c,d]
Commercial 7.9% dispersed Ir/γ-Al$_2$O$_3$	3950 ± 1000 [b,c]	410,000 [b,c]
$[Ir(0)]_n$ (from $[Ir(1,5\text{-}COD)CH_3CN)_2]BF_4$ plus H$_2$)	3900 ± 600 [b,c] (780 ± 730) [c,e]	51,600 [b,c]
$Ir(0)_{\sim 300}$ · polyoxoanion nanoclusters	3200 ± 1000 [f,g] (1100 ± 500) [h,g]	18,000 [d]
$(Bu_4N^+)_9[P_2W_{15}Nb_3O_{62}]$ (zero Ir control reaction)	0	0

[a] Standard conditions were employed for these hydrogenations (i.e., 22.0°C, 1.65 M purified cyclohexene and 40 psig H$_2$) [7], except that Baker acetone distilled from K$_2$CO$_3$ was used as solvent in these particular experiments [8]a. Note of course that to the extent different rate laws for these catalysts are operative under the specific conditions employed, then these rate comparisons involve a comparison of the relative efficiencies of *different mechanisms* (but under identical conditions).

[b] These data [7] were originally reported in Edlund's Ph.D. thesis [8]a.

[c] All runs are from a single batch of material; turnover numbers are corrected for the number of exposed Ir(0).

[d] Done under conditions where a maximum of 80,000 turnovers were possible (i.e., the catalyst became deactivated after the number of turnovers indicated).

[e] Runs from multiple batches; turnover numbers are deliberately not corrected for the exposed Ir(0) surface area so as to reveal the expected large variability in the surface area of the Ir(0) precipitates (i.e., the ±94% error bars).

[f] Calculated in this case from TON = $\{-d[H_2]/dt_{initial}$ (in mmol H$_2$/h)$\}/(0.2 \times 0.0035$ mmol catalyst), where 0.2 is the correction for the fraction of Ir(0) atoms that are active from PPh$_3$ poisoning studies. The error bars in $\{-d[H_2]/dt_{initial}\}$ are small (i.e., typically ⩽ 10%), so that the major error is in the estimate of the fraction (0.2) of the total Ir(0) that are active.

[g] Calculated as in footnote f above but estimating a 0.5 fraction (i.e., 50%) of Ir on the surface using an idealized Ir$_{309}$ nanocluster model (see elsewhere for additional detail [7], [8]a).

[h] These entries used Burdick and Jackson acetone.

provided elsewhere [7], and reverified as part of the present work, shows a loss of only 6% (in the best case to date) of catalytic activity upon cycles of isolation, then redissolving and retesting the catalytic activity. Specifically, following generation of the catalyst from **1** under H$_2$ and ca. 7000 subsequent turnovers, the $Ir(0)_{\sim 300}$ nanoclusters were isolated, dried under vacuum at 25°C overnight, and then redispersed in fresh acetone (along with fresh cyclohexene; i.e., all as before [7]). The observed catalytic activity actually increases slightly ($\sim$ 10%). If the cycle of catalyst isolation, then reuse with fresh acetone and cyclohexene is repeated, the catalytic activity now drops from a *relative* rate of 1.0 to 0.54, representing a decrease in activity of ca. 46% in this particular run. (Previously, the activity dropped 42%, from a relative rate of 1.0 to 0.58, in a closely analogous but not identical experiment; see Table 2, entries/cycles 2–3, and absolute numbers 1.7 to 1.0 elsewhere [7]).

The composition and structure of the deactivated form of the catalyst is unknown presently, but is under active investigation, as it likely

holds key insights into how to prepare an even longer lived catalyst. In addition, more detailed kinetic and mechanistic studies of cyclohexene hydrogenation by these $Ir_{\sim 300}$ · polyoxoanion nanoclusters are in progress. However, the key initial finding is that the catalytic activity for olefin hydrogenation of the $Ir_{\sim 300}$ · polyoxoanion nanocluster catalysts *is as high—essentially the same within experimental error—as observed for any of the Ir(0) catalysts tested, and is without precedent in terms of catalyst lifetime for a non-polymer protected, nanocluster-catalyzed reaction in solution.*

Also noteworthy is the fact that ours is only the second nanocluster system where mechanistic evidence has been presented which convincingly argues that the nanocluster (or, possibly, nanocluster fragments) are the true catalyst [7] (i.e., second following the Moiseev and coworkers' $Pd_{\sim 570}$ work [35]). We also report the apparent, previously undocumented rate-accelerating effects of H$_2$O and H$^+$, further studies of which are in progress. Preliminary evidence suggests that the H$^+$ effect is at least in part due

to a little precedented H$^+$-assisted reductive elimination pathway. [25] Such a finding of an apparent little-appreciated elementary step for metal particle catalysts is ostensibly a somewhat profound finding [26], one that is, however, not inconsistent with the relatively poor level of true mechanistic understanding in heterogeneous catalysis—even for this early and arguably 'best studied' catalytic reaction! This finding also attests to the significance of having metal-particle catalysts, such as Ir$_{\sim 300}$, that are soluble and stable—yet reactive—so that they can be studied *in solution*.

3.4. Nanocluster solution stability studies

As has been noted, the stability of the Ir$_{\sim 300}$ · polyoxoanion nanoclusters is quite high in comparison to traditional colloids—for example, it is sufficient to allow their isolability, storage in a bottle, and subsequent use as a reagent. To probe this crucial issue further, their stability in solution and at temperatures above 25°C was examined in control experiments. At 50°C, a clear amber acetone solution of the nanoclusters turned a fainter amber, and a dark-brown precipitate of Ir(0) formed within ca. four days. Interestingly, and consistent with the literature, the thermal stability of the Ir(0)$_{\sim 300}$ nanoclusters *decreases* in the presence of 1.65 M cyclohexene, presumably due to displacement of the anionic and thus stabilizing polyoxoanion by the neutral, destabilizing olefin [9]j. Hence, even the present isolable Ir$_{\sim 300}$ · polyoxoanion nanoclusters are still only metastable, as one might have expected given the literature of colloids and nanoclusters cited

above. This is clearly the *most significant limitation* of these (and all other reported) nanocluster catalysts, a limitation that must, therefore, be a focal point of future research efforts. We note, however, that the literature reveals many colloids that are formed in, and thus stable to, 100°C water. In addition, a recent report describes Pd nanoclusters stabilized against bulk metal precipitation by propylene carbonate as solvent (and, we'd add, Cl$^-$ ligands plus Na$^+$ counter cations) to 140–155°C! Note, however, that the needed TEM studies to see if any agglomeration is occurring were not reported nor were any controls checking to see if the propylene carbonate retains its integrity under the reaction conditions [32]f. The trick, then, will be to find polyoxoanions or other ligands that allow *both* of the seemingly mutually exclusive properties of high stability *and* high catalytic activity (i.e., ligands which do not fully poison the nanocluster's surface, a well-established phenomenon (e.g., see p. 103–104 elsewhere [9]l)).

In a related sense, Schmid's recent report of ligand-stabilized nanoclusters is very important [9]k,l. They show, after immobilization on a carbon support [27], a remarkable sensitivity in the selectivity to seemingly minor changes in the ligands (see Fig. 7d and the discussion on page 592 elsewhere [9]k,l). Hence, this work presages the development of a new sub-area of nanocluster catalysis, that of highly selective, ligand-modified nanoclusters.
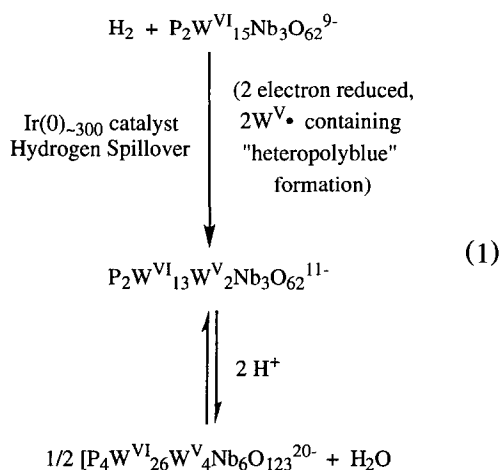
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[25] J.D. Aiken III and R.G. Finke, unpublished results.

[26] That is, it is striking that, even in our first nanocluster reaction and mechanism study, one on catalysis' arguably best studied reaction, hydrogenation, we have *already* found a little-appreciated elementary step: H$^+$-assisted reductive-elimination. This reaction almost surely also occurs in heterogeneous catalysis, as it explains, for example, why protic solvents like EtOH or HOAc are often preferred in heterogeneous hydrogenations.

[27] An active issue is whether or not one is best off to simply immobilize one's nanoclusters, that is, to use them to prepare better particle size- and composition-controlled heterogeneous catalysts. Schmid argues "yes" for this [9]k,l, since only the Moiseev and co-workers Pd$_{\sim 570}$ clusters and our Ir(0)$_{\sim 300}$ have been shown to be stable enough for cycles of catalysis in solution. Other workers have also adopted the 'solid-oxide-supported namoclusters' approach [11]b, [32]e. However, for kinetic and mechanistic studies, the answer is clearly "no", as kinetic and spectroscopic studies are at least easier if not more powerful in solution. In the long term, however, practical catalysis often means immobilized catalysts, and Professor Schmid's "yes" answer may prove true.

3.5. Observation of spillover of hydrogen to and from the polyoxoanion support

As cyclohexene hydrogenation catalyzed by the $Ir_{\sim 300}$ · polyoxoanion nanocluster proceeds, the solution turns a deep blue. This is an easily interpreted result, since reduction of W^{VI}-containing polyoxoanions is known to form W^{V}-containing *blue* complexes, the well-known '*heteropolyblues*' [47]. Titration of the blue solution with the one-electron oxidant Ce^{4+} [i.e., using $(NH_4)_2Ce^{IV}(NO_3)_6$, in 0.1 N H_2SO_4 to stabilize the Ce^{4+}; see elsewhere for details [6]a reveals that a *2 electron reduced, heteropolyblue form* of the polyoxoanion has been formed, $P_2W_{13}^{VI}W_2^{V}Nb_3O_{62}^{11-}$ (which is present as its Nb–O–Nb bridged-form from the reaction: $2H^+ + 2P_2W_{13}^{VI}W_2^{V}Nb_3O_{62}^{11-} \rightarrow 1$ $H_2O +$ $P_4W_{26}^{VI}W_4^{V}Nb_6O_{123}^{20-}$). Control experiments, using the 7.9% dispersed 1% Ir/γ-Al$_2$O$_3$ catalyst plus authentic unreduced, white $P_4W_{30}^{VI}Nb_6O_{123}^{16-}$ (as its $[(Bu_4N)_{12}H_4]^{16+}$ salt [3]b), confirm that the polyoxoanion is readily reduced by 40 psig H_2 to its deep blue, heteropolyblue form—that is, in one sense this is just the straightforward reduction of the molecular, polyoxoanion species by H_2. In another view, this is the first discrete example of 'hydrogen spillover' [48,49] in a soluble, molecular oxide support, Eq. 1.

$$H_2 + P_2W^{VI}{}_{15}Nb_3O_{62}{}^{9-}$$

Ir(0)$_{\sim 300}$ catalyst
Hydrogen Spillover

(2 electron reduced, 2W^{V}• containing "heteropolyblue" formation)

$$P_2W^{VI}{}_{13}W^{V}{}_2Nb_3O_{62}{}^{11-}$$ (1)

2 H$^+$

$$1/2\ [P_4W^{VI}{}_{26}W^{V}{}_4Nb_6O_{123}{}^{20-} + H_2O$$

What makes this well-defined example of

hydrogen spillover of interest is that, in contrast to hydrogen spillover onto at least some of the solid oxides of heterogeneous catalysts, the form $(H_2 \rightarrow 2H^+ + 2e^-)$ and site $(2W^{VI} + 2e^- \rightarrow 2W^{V}\cdot)$ of the spilled-over hydrogen are *exactly and unambiguously defined*. This is true since the 2 e^- reduced, 2 $W^{V}\cdot$ containing, polyoxoanion structure and reduction site is exactly and unambiguously defined by the extensive studies of heteropolyoxoanion blues [47].

Of further interest is the observation that the spillover is reversible. Releasing the 40 psig H_2, and placing the blue catalyst solution under N_2, causes the blue color to fade completely within $\geqslant 0.5$ (to several) h; that is, the spilled-over H^+ and e^- apparently rapidly reform and evolve H_2 ('reverse spillover' [48], [49]c). Replacing the $Ir_{\sim 300}$ · polyoxoanion nanoclusters under H_2 again causes the formation of heteropolyblue, demonstrating the reversibility of spillover through multiple cycles of reduction / reoxidation. The $Ir_{\sim 300}$ · polyoxoanion system and its associated reduction of the soluble, polyoxoanion oxide is, to our knowledge, the first molecular analog of the well known and commercially important [28], but generally still poorly understood, spillover of H_2 onto solid-oxide supports [48]a–c, [49]. More specifically, the observed reduction of the polyoxoanion support is a discrete analog of the well-known formation, via hydrogen spillover, of tungsten-oxide hydrogen-blue and bronze phases, H_xWO_3 [49].

4. Conclusions and future directions

The first member of a new subclass of nanocluster catalysts, polyoxoanion- and Bu_4N^+-stabilized nanoclusters, reveals five interesting

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[28] The significance of H · spillover is attested to by the following quote from the literature on spillover [18]a: "Spillover... is a phenomenon of wide if not universal occurrence with supported catalysts, and one of the least well understood effects. Its importance cannot be overstated".

points relevant to catalysis by these new catalyst materials: (i) the $Ir_{\sim 300}$ · polyoxoanion catalysts are indeed quite active for the prototypical structure-insensitive catalytic reaction, cyclohexene hydrogenation; (ii) the rate per exposed Ir(0) is as high as any Ir(0) heterogeneous catalyst tested; and (iii) the catalyst lifetime in solution without polymeric protectants (18,000 turnovers, 25°C, 10 days) is unprecedentedly long. But, (iv) the loss of some activity (40–50%) in cycles of isolation/redissolving of the $Ir_{\sim 300}$ · polyoxoanion nanoclusters and the limited, $\leqslant 50°C$ thermal stability are presently major limitations of these soluble heterogeneous catalysts (and are, therefore, a central target of research in progress). Also of interest is (v) the reduction of the polyoxoanion support, $H_2 \rightarrow 2H^+ + 2e^-$; and $2W^{VI} + 2e^- \rightarrow 2W^{V}$, a process that provides a discrete, soluble analog of the well known spillover of H_2 onto solid-oxide supports such as WO_3. Particularly noteworthy is (v) that the present $Ir_{\sim 300}$ · polyoxoanion nanoclusters are unique in terms of their combination of (a) isolability, (b) well-defined composition, and yet (c) high catalytic activity and relatively long catalytic lifetimes in solution.

Overall, it is clear that hybrid homogeneous–heterogeneous, nanocluster catalysis is an area of considerable interest for further studies. Our own future publications will detail our efforts at increasing the thermal stability of polyoxoanion- and R_4N^+-stabilized nanoclusters, at scaling up the best syntheses of the most stable, yet most active, nanoclusters, of Rh(0), Pd(0), Pt(0) and other nanoclusters, as well as catalytic reaction survey and associated kinetic and mechanistic studies. We will also be reporting our now complete kinetic studies of the mechanism of formation of $Ir(0)_{\sim 300}$ · polyoxoanion nanoclusters from the discrete precatalyst $[(1,5-cyclooctadiene)Ir \cdot P_2W_{15}Nb_3O_{62}]$, **1**, and under H_2. That work that holds considerable insight into central issues such as size control, magic numbers in nanocluster syntheses, or rational synthesis of *initially known structure* bimetallic (alloy) and

higher multimetallic nanoparticles [6]b. An important question is whether such detailed studies of nanocluster catalysts can help address our long term, ultimate goal of adding near-atomic level composition, structural and mechanistic information [29] [50] to the concepts [51] of metal particle catalysts.

Acknowledgements

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