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Nanocluster Formation and Stabilization Fundamental Studies:[†] Investigating “Solvent-Only” Stabilization En Route to Discovering Stabilization by the Traditionally Weakly Coordinating Anion BF_4^- Plus High Dielectric Constant Solvents

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The nanocluster literature contains a wide variety of nanocluster stabilizing agents. In addition to the plethora of putative stabilizing additives, 12 claims appear of “solvent-only” stabilization of transition-metal nanoclusters—a hypothesis that is tested for the first time as part of the present studies. When the two main modes of nanocluster stabilization, electrostatic and steric are considered, “solvent-only” stabilization can only be steric (i.e., is not electrostatic). Solvent-only stabilization would, therefore, require that a strongly coordinated, perhaps even kinetically nonlabile, solvent be present on the nanocluster surface. Hence, an investigation has been conducted into potential sources for the stabilization of prototype $Ir(0)_n$ transition-metal nanoclusters prepared from $[(1,5\text{-COD})Ir(CH_3CN)_2][BF_4]$ in five different solvents, with a special focus on the formulation and testing of alternative hypotheses regarding the true source of the nanocluster stabilization in putative solvent-only stabilization conditions. Seven total hypotheses are tested with five being initially ruled out; they are, namely, stabilization by (i) trace chloride (ii), surface hydrides, (iii) scavenged charge, (iv) solvent oxidative addition reactions with the nanocluster surface, or (v) polymerized solvent. This led in turn to two additional main alternative hypotheses: (vi) nanocluster surface ligation by high-donor number solvents (i.e., in the absence of anions) and (vii) nanocluster stabilization by surface-coordination of the traditionally weakly coordinating anion BF_4^-. Our results reveal a significant contribution to nanocluster stability from the traditionally weakly coordinating BF_4^- in high dielectric constant solvents, such as propylene carbonate. Literature claims of solvent-only nanocluster stabilization are not supported by our findings. Overall, DLVO (Derjaugin–Landau–Verwey–Overbeek) theory of colloidal stability is supported and found to apply to even traditionally weakly coordinating anions.

Introduction

Transition-metal nanoclusters have received a great deal of interest because of their perceived importance in several areas of science, including, but not limited to, catalysis,[1] chemical sensors,[2] and quantum computers.[3] To realize these and other potential applications, the requisite nanoclusters should ideally be “bottleable” and redissolvable, that is, one should be able to prepare, isolate, weigh out, and fully redisperse identical samples of reproducible nanoclusters.[4] This in turn means that understanding the topic of transition-metal nanocluster *stabilizers* is of considerable fundamental importance.

However, as recently stated, “the (nanocluster) literature contains a dizzying variety of stabilizing agents.”[1f] Additionally, there are at least 12 claims of nanoclusters prepared without added stabilizing agents or “solvent-only” stabilized nanoclusters.[5−14] Separately, others have noted that, for transition-metal nanoclusters, “people in general cannot understand...which preparation method is the best among those proposed.”[15] In short, the myriad of stabilizers appearing in the literature is hindering the progress of nanocluster science. For this reason, since 2002 we have been evaluating the efficacy of putative nanocluster stabilizers,[16,17] with an emphasis on catalytically active nanoclusters.[18]

DLVO Theory and Nanocluster Stabilization. DLVO (Derjaugin−Landau−Verwey−Overbeek) theory[19] was developed in the 1940s to describe how colloids are stabilized.[20] DLVO theory relies on anions adsorbed to the coordinatively unsaturated, electrophilic surface of nanocolloids to achieve

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[†] Part VII in a series. For parts I−VI, see refs 16, 17, 24, 47, 64, and the review cited in reference 63.

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Columbic repulsion between particles.[21] The electrostatic repulsion opposes van der Waals attractions that would otherwise lead to particle agglomeration and precipitation. Hence, DLVO-type stabilization is also commonly referred to as *electrostatic stabilization*. Anions in excess of those adsorbed onto the nanocluster surface compose the diffuse multilayer of ions surrounding the nanoclusters; this diffuse layer is referred to as the Debye layer (denoted by $1/\kappa$; values are typically in nanometers) depicted in eq 1.

$$1/\kappa = ((\epsilon_0 \epsilon_R kT)/\sum_i (z_i e)^2 c_{i_0})^{0.5} \tag{1}$$

In eq 1, ϵ_0 is the permittivity of free space, ϵ_R is the dielectric constant of the medium (the solvent), k is the Boltzman constant, T is the temperature, z_i is the ion valency, e is the charge on an electron, and c_{i_0} is the concentration of the ion species, i, in the bulk solution.[22] Two predictions of DLVO theory and eq 1 are especially important for the studies herein: (i) that *ions* are necessary for the stability of nanocluster systems and in the absence of steric stabilizers, and (ii) that a thicker Debye layer (and hence more stable nanoclusters) will be formed in *high dielectric constant* solvents if a layer of adsorbed anions is present along with an excess of anions available for the diffuse layer. The other general source of colloidal stabilization is steric stabilization,[23] repulsion between sterically bulky ligands coordinated to the nanocluster surfaces[24] (see Scheme 5 in ref 63).

Current Status of Methods for Measuring Nanocluster Stability. A general problem in the area of transition-metal nanocluster stabilization is that no standard method exists to assay "stability". Indeed, nanocluster stability is not even an operationally well defined term, so that an assessment of stability is presently at the discretion of individual research groups. A survey of the nanocluster literature reveals that stability is often declared on the basis of a (ex situ, solid state) transmission electron microscopy (TEM) image alone! Even then it is not clear if the images shown are representative; as a specific example, of 60 preparations of $Pt(0)_n$ nanoclusters examined elsewhere, only 4 report a yield of nanoclusters, and fewer report if bulk metal was formed (as was found in control experiments reported subsequently).[25]

Examination of the colloidal/nanocluster literature reveals that only two methods are available for evaluating classical water-soluble colloidal stability:[26,27] these methods, which were used for gums, other ill-defined additives, or polymers, are 41 and 105 years old, are qualitative, and are applicable only to Au colloids in water.[27,28] Additionally, these two methods only visually assay stability qualitatively based on the color change observed upon agglomeration of Au colloids

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(21) In neutral metal nanoclusters, anions are attracted to the coordinatively unsaturated, electrophilic nanocluster surfaces. Adsorption of these anions induces an electrostatic charge mirror, resulting in a partial positive charge (mirror) on the nanocluster surface.[19,22] The resulting particles with surface-bound anions are anionic in nature and repel each other; this Coulombic repulsion is a key component of DLVO-type electrostatic stabilization.[19]

(22) Evans, D. F.; Wennerström, H. *The Colloidal Domain*, 2nd ed.; Wiley-VCH: New York, 1999.

(23) Some authors claim "non-DLVO" forces, such as hydration, structural, oscillatory, hydrophobic, depletion, fluctuation, and protrusion forces. However, these forces are generally believed insufficient to be the sole source of stabilization.[20]

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in water. Hence, a modern operational definition of nanocluster stability, plus a method for assaying relative stabilities, is needed.

Reflection on the above point and the relevant literature[26−28] teaches that the preferred method and thereby operational definition is a kinetic measurement of stability based on the *quantitative rates of agglomeration* of nanoclusters. It is noteworthy that nanocluster agglomeration is expected to be a complex, subtle interplay of multiple phenomena such as chemical bond formation, structural reorganization, and sometimes reversible agglomeration.[29] Efforts have been underway in our labs to provide the kinetic methods necessary to measure agglomeration rates; these studies are still in progress.[30]

In the absence of a general kinetic method to assay nanocluster agglomeration under any solvent, temperature, or other condition, the one method available in the literature at present for ranking the *formation* and *stabilization* of transition-metal nanoclusters is the 5 criteria method developed in our labs in 2002.[16,17] The 5 criteria are as follows: (i) the level of kinetic control during the nanocluster formation reaction as measured by the k_2/k_1 ratio of autocatalytic surface growth (k_2) to nucleation (k_1), larger values indicating a high level of kinetic control; (ii) the nanoclusters' size distribution as determined by TEM (less than or equal to ±15% being defined as "near-monodisperse" nanoclusters);[4] (iii) the ability to isolate from solution and ideally bottle the nanoclusters for future use without their agglomeration to bulk metal; (iv) the catalytic activity of the isolated nanoclusters once redissolved in solution with fresh cyclohexene substrate; and (v) the total catalytic lifetime for cyclohexene hydrogenation observed for the nanoclusters in solution. The perhaps single most stringent test of claimed nanocluster stabilizers is criteria (iii), the formation of isolable and subsequently redissolvable nanoclusters while seeing if bulk metal is formed.

We first used the 5 criteria method to rank anionic stabilizers, anions being expected to be a key by DLVO theory (recall eq 1). The 5 criteria method, while admittedly not perfect (e.g., lacking a kinetic measurement of agglomeration) and not yet applicable in every desired situation,[31] is nevertheless a welcome advance in an area where no modern methods previously existed to rank nanocluster stabilizers.

Claims of Solvent-Only Stabilized Nanoclusters. A belief in the literature of modern transition-metal nanoclusters directly relevant to the present work is that *solvent-only* stabilized nanoclusters exist.[5−14] The concept of solvent-only nanocluster stabilization is attractive since such nanoclusters, if they exist, would have their surfaces sites ready for catalysis via only a dissociation of weakly coordinated solvent—a perhaps ideal solution to what we have coined as the "naked nanocluster problem" of nanocluster catalysis.[32] By definition, such putatively solvent-only stabilized nanoclusters should not possess surface-coordinated anions;[19] in other words, putative solvent-only stabilization is, in its essence, little-precedented "anti-DLVO theory" stabilization. Table S1 of the Supporting Information provides further details on the literature's 12 claims of solvent-only stabilized nanoclusters.

The solvent-only stabilization hypothesis has not been previously subjected to attempts to disprove it,[33] despite at least 12 papers claiming to have made solvent-only stabilized nanoclusters. For example, an early paper claims to have prepared "$Ti(0)_n$•THF" and "$Zr(0)_m$•THF" colloids;[5a] however, the authors ignore the 8.5% Cl^- present by elemental analysis that is expected to provide electrostatic DLVO-type stabilization. (Later contributions by the same group preparing alkylammonium halide stabilized nanoclusters do, however, recognize the role of anions, and specifically Cl^-, as stabilizers.)[34,35] Hypothetical $Ti(0)_n$•THF and $Zr(0)_m$•THF colloids would also be highly air-sensitive[36] with an oxide surface coating possible as a stabilizer.

As a second example of putative solvent-only stabilization, propylene carbonate is the claimed stabilizer in a system of electrochemically generated Pd colloids.[11] However, those authors did not consider two key alternative hypotheses for stabilization, namely, (i) that Cl^- from the NaCl electrolyte is probably contributing to the stability via electrostatic, DLVO-type stabilization, or (ii) that the 5% ethanol in the PC solution might be contributing to the stability by ligating the nanocluster surface, possibly in its deprotonated alkoxide form.[11]

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(31) A referee has raised the good point that stabilization requirements may well change versus nanocluster size and, thus, during nanocluster development. We agree; in fact, elsewhere we provide evidence for a particle-size-dependent metal−ligand surface coverage/bond dissociation energy[25] that supports the general notion of particle-size-dependent stabilization effects.

(32) The "naked nanocluster problem",[32b,c] perhaps more accurately called the "ligand-labile nanocluster problem" is the need for efficient high-yield syntheses of metastable nanoclusters that have relatively easily removed ligands so that they can be used for low-temperature syntheses of novel heterogeneous catalysts or other applications of clean, ideally naked-surface nanoclusters. In practice, completely naked nanoclusters will likely not be achievable (since even alkane metal−ligand bond energies can be 10 ± 3 kcal/mol)[32d] so that approaches that parallel precedent such as Wilke's "naked nickel",[32e] Ni(1,5-COD)$_2$, with stabilizing but displaceable ligands are what is needed here. (b) Özkar, S.; Graham, C. R.; Finke, R. G. Unpublished results and experiments in progress**.** (c) Recent efforts to completely remove polymeric poly(vinylpyrrolidone) stabilizers from $Pt(0)_n$ nanoclusters with heat treatments, e beams, O-atom beams, or H_2/O_2 treatments were unsucessful. Kim, F.; Connor, S.; Song, H.; Kuykendall, T.; Yang, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 3673; Song, H.; Kim, F.; Connor, S.; Somorjai, G. A.; Yang, P. *J. Phys. Chem. B* **2005**, *109*, 188; Rioux, R. M.; Song, H.; Hoefelmeyer, J. D.; Yang, P.; Somorjai, G. A. *J. Phys. Chem. B* **2005**, *109*, 2192; Song, H.; Rioux, R. M.; Hoefelmeyer, J. D.; Komor, R.; Niesz, K.; Grass, M.; Yang, P.; Somorjai, G. A. *J. Am. Chem. Soc.* **2006**, *128*, 3027. (d) Yang, G. K.; Peters, K. S.; Vaida, V. *Chem. Phys. Lett.* **1986**, *125*, 566; Simon, J. D.; Xie, X. *J. Phys. Chem.* **1989**, *93*, 291−293; Morse, J. M., Jr.; Parker, G. H.; Burkey, T. J. *Organometallics* **1989**, *8*, 2471. (e) Fischer, K.; Jonas, K.; Misbach, P.; Stabba, R.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 943; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 185.

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There are some isolated reports of nanoclusters prepared in the absence of anions, where truly solvent-only stabilized nanoclusters are at least conceivable. Chaudret et al. have reported a well-designed halide-free precursor, Ru(COD)(COT) (COD = 1,5-cyclooctadiene; COT = cyclooctatriene), to prepare $Ru(0)_n$ nanoclusters. However, frequently other potentially stabilizing entities are present such as alcohols,[6,10] long-chain amines,[37] or polymers.[38] Consequently, these systems, too, cannot be considered strictly solvent-only stabilized. Another precursor that appears to be ideal for studying solvent-only stabilization is $Pd_2(dba)_3$[39] (where dba is dibenzylidene acetonate). 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,[39] a potential if not obvious stabilizer. The surface layer of carbon means that the nanoclusters prepared in this study are also not truly solvent-only stabilized. Therefore, *even with these two seemingly ideal nanocluster precursors, there is confusion as to whether solvent-only stabilized nanoclusters actually exist.* Note also here that "solvent" may be a nanocluster ligand, may provide general solvent effects (e.g., on the $1/\kappa$ of DLVO theory as noted in eq 1), or both. In short, testing if solvent-only stabilized nanoclusters truly exist is an important goal in the understanding of the factors that stabilize modern transition-metal nanoclusters.

Present Study. Herein, using the 5 criteria method, along with the scientific method of multiple alternative hypotheses and attempted disproof of each hypothesis,[33] we evaluate the formation and stabilization of $Ir(0)_n$ nanoclusters prepared from $[(1,5\text{-COD})Ir(CH_3CN)_2][BF_4]$ in five solvents[40] (see Table 1). Five alternative hypotheses for solvent-only stabilization have been investigated and ruled out en route to the main two alternative hypotheses investigated: (i) stabilization by solvent ligation of the nanocluster surface by high donor-number[41] (DN) solvents and (ii) DLVO-type stabilization by the BF_4^- anion with a dielectric constant solvent. These main two alternative hypotheses will be investigated first in what follows.

Results and Discussion

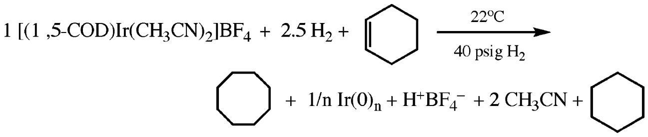
Testing the Solvent-Only Stabilized Nanoclusters Hypothesis. Preparation of $Ir(0)_n$ Nanoclusters in the Absence of Anionic Stabilizers. As an initial test of the solvent-only stabilization hypothesis, we prepared $Ir(0)_n$ nanoclusters as before[17] from the precursor $[(1,5\text{-COD})Ir(CH_3CN)_2][BF_4]$, but this time without Proton Sponge (PS, 1,8-bis(dimethylamino)naphthalene) so that relatively little potentially stabilizing anion would be present, Scheme 1. This follows because without a base like PS, more of the conjugate acid is formed, $H^+BF_4^-$ (or more generally H^+Y^-), rather than primarily the potentially stabilizing anion BF_4^- with a PS$-H^+$ countercation (or, more generally, $Y^-/PS-H^+$). PS has been shown to be a preferred H^+ scavenger in nanocluster syntheses,[17] Scheme 2, one that does not serve as a good ligand because of its steric bulk.

Table 1. Five Solvents Studied Herein,[42] Their Dielectric Constants (ϵ), and Donor Numbers (DN; the solvent donor number is a measure of Lewis basicity)[41]

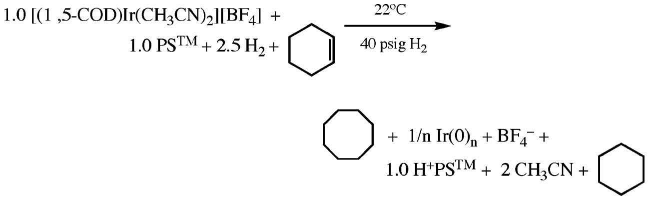
solvent (abbreviation)	ϵ	DN
N-methylacetamide (NMA)	165	(27.8) [a]
propylene carbonate (PC)	69	15.1
acetonitrile (CH_3CN)	39	14.1
N-methylpyrrolidinone (NMP)	30	27.1
acetone	20	17.0

[a] This value is the donor number from the structurally similar dimethylacetamide because a donor number for NMA itself is not yet available in the literature.

Scheme 1. Generalized $Ir(0)_n$ Nanocluster Formation Reaction without Proton Sponge



Scheme 2. Generalized $Ir(0)_n$ Nanocluster Formation Reaction in which the Only Anion Present Is BF_4^-



To follow the kinetics of nanocluster formation (i.e., to obtain the k_1 and k_2 parameters that are part of the 5 criteria method),[16,17] we again used the cyclohexene reporter-reaction kinetic method.[43,44] This method exploits the fact that the cyclohexene hydrogenation reaction is much faster than the nanocluster formation reaction and, hence, can be used to indirectly, but powerfully and in real time, monitor the kinetics of nanocluster formation.[43] The hydrogen uptake curves for nanocluster formation are converted to cyclohexene consumption curves using the known 1:1 H_2/cyclohexene stoichiometry, and the kinetic data are then fit by the established 2-step mechanism for nucleation (k_1) and autocatalytic surface-growth (k_2) kinetic parameters for transition-metal nanocluster formation[43,44] (see the Experimental Section for further details).

Any stabilization observed under the conditions and resultant reaction in Scheme 1 would, therefore, have to come

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(37) Pery, T.; Pelzer, K.; Buntkowsky, G.; Philippot, K.; Limbach, H.-H.; Chaudret, B. *ChemPhysChem* **2005**, *6*, 605.

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(39) Dhas, N. A.; Cohen, H.; Gedanken, A. *J. Phys. Chem. B* **1997**, *101*, 6834.

(40) Since DLVO theory[19] remains the only predictive tool for colloidal stability (and predicts solvent effects based solely on ϵ), we initially chose for study the solvents in Table 1 herein because of their widely varying dielectric constants.

(41) Gutmann, V. *Coord. Chem. Rev.* **1976**, *18*, 225.

(42) We intended to study nitromethane (ϵ = 36), but it appears to be deprotonated by PS, leading, in turn, to an undetermined, inactive, brown species in the reaction solution before the solution was exposed to H_2 (see Figure S1 of the Supporting Information).

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Table 2. Five Criteria Evaluated for $Ir(0)_n$ Nanoclusters in Five Solvents with $H^+BF_4^-$, BF_4^-, and $1\text{-}MeCB_{11}F_{11}^-$

	solvent	ϵ	counterion	k_1 (h^{-1})	k_2 ($\times 10^{-3}$ h^{-1} M^{-1})[a]	k_2/k_1 ($\times 10^{-5}$ M^{-1})[a]	d_m (Å)	appearance	redispersible	cat act[b]	TTO[c]
1	NMA	165	$H^+BF_4^-$			poor fit[d]		clear, metal[e]	no		
2	NMP	36	$H^+BF_4^-$			poor fit[d]		clear, metal[e]	no		
3	PC	69	$H^+BF_4^-$			poor fit[d]		clear, metal	no		
4	NMA	165	BF_4^-	0.98(8)	7.9(4)	0.081(8)	aggregated	brown	partially	0.88(5)	[62,500]
5	PC	69	BF_4^-	1.1(1)	7(1)	0.070(4)	aggregated	brown	partially	0.083(5)	[45,600]
6	CH_3CN	39	BF_4^-	0.11(1)	3.6(2)	0.34(5)		clear, metal	no		
7	NMP	36	BF_4^-	0.18(1)	8.9(4)	0.49(3)		brown, metal	no		
8	acetone	20	BF_4^-	0.052(5)	12.1(2)	2.4(2)		clear, metal	no		
9	PC	69	$1\text{-}MeCB_{11}F_{11}^-$	0.46(5)	6.0(5)	0.20(3)		clear, metal	no		

[a] The values for k_2/k_1 have been corrected by the mathematically required stoichiometry factor of 1400 as detailed elsewhere.[43] [b] In units of mmol H_2/h. [c] Total turnovers of cyclohexene hydrogenation (mol product/mol catalyst); brackets indicated that bulk metal was formed during the course of these experiments, so these values are necessarily an upper limit on the true nanoparticle TTOs. [d] A poor fit to the 2-step mechanism was observed for these data. [e] These solutions initially appear black, but close inspection reveals a clear solution with finely divided particles plus bulk metal on the stir bar and culture tube.

from strong, presumably approaching kinetically nonlabile, solvent coordinated to the nanocluster surface. Because the coordinatively unsaturated electrophilic nanocluster surface is Lewis acidic, one expects that higher donor-number solvents would, therefore, be preferred for preparing "solvent-only stabilized" nanoclusters.

We attempted three nanocluster syntheses under the conditions in Scheme 1 in *N*-methylacetamide (NMA), *N*-methylpyrrolidinone (NMP), and propylene carbonate (PC) (entries 1–3 in Table 2) since these three solvents provide the better donor number and dielectric constant values. Note also that the donor number changes by a factor of ~2 in this series. However, reduction of $[(1,5\text{-}COD)Ir(CH_3CN)_2][BF_4]$ in all three solvents *yielded clear and colorless solutions* (i.e., bulk metal instead of nanoclusters). Hence, solvent-only stabilization through solvent ligation of the nanocluster surface by high-donor number solvents does *not* afford stable $Ir(0)_n$ nanoclusters. These experiments, the first carefully designed to remove the stabilization effect of coordinating anions while different donor number solvents are tested as putative stabilizers, do not support the claims of solvent-only stabilized nanoclusters.

Investigation of Contributions to Nanocluster Stabilization from the Traditionally Weakly Coordinating Anion BF_4^-. Preparation of $Ir(0)_n$ Nanoclusters in the Presence of BF_4^-. In the next series of experiments, PS was added to $[(1,5\text{-}COD)Ir(CH_3CN)_2][BF_4]$ such that the BF_4^- anion is formed instead of the conjugate acid $H^+BF_4^-$, Scheme 2.

An examination of entries 4–8 in Table 2 reveals that, with BF_4^- present as the only possible anionic stabilizer, only the two solvents with the highest dielectric constants studied, NMA and PC (ϵ = 165 and 69, respectively), afforded homogeneous brown solutions characteristic of $Ir(0)_n$ nanoclusters.[45] The other three lower ϵ solvents yielded clear solutions with bulk metal present instead of nanoclusters (see the Supporting Information for details). The resulting implication, then, is that the traditionally weakly coordinating BF_4^- plus high ϵ solvents is sufficient to provide metastable nanoclusters. Recent XPS evidence from Dupont and coworkers confirms that the traditionally weakly coordinating PF_6^- anion is present on the surface of a sample of dried nanoclusters (the PF_6^- being the anionic component of the ionic liquid 1-butyl 3-methylimidazolium hexafluorophosphate employed in that study).[46] A specific hypothesis for how BF_4^- and PF_6^- can coordinate to, and thereby stabilize, transition-metal nanoclusters is the tridentate surface-binding mode postulated elsewhere.[47] Also probably key in how even traditionally weakly coordinating anions such as BF_4^- or PF_6^- can provide nanocluster stabilization in polar solvents, is the *up to 2-fold* stronger metal–ligand bond dissociation energies in nanoclusters than the corresponding bulk metal, thermodynamic effects identified elsewhere[25,48] which result in a particle-size-dependent fractional ligand coverage of nanocluster surfaces.[25]

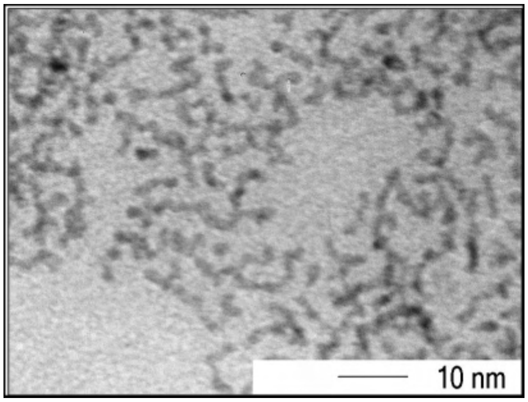

Figure 1. TEM micrograph (580 000 magnification) of agglomerated $Ir(0)_n$ nanoclusters prepared in PC in the presence of 1 equiv of BF_4^-.

Nanoclusters prepared in NMA and PC (entries 4 and 5 in Table 2) were examined using TEM for criteria (ii) of the 5 criteria method. A representative image of nanoclusters prepared in PC is shown in Figure 1. This micrograph is qualitatively useful, allowing the direct observation of agglomerated nanoclusters, but the extensive agglomeration eliminates any hope of quantifying the size and size distribution of the nanoclusters. Attempts to isolate nanoclusters prepared under the conditions of Scheme 2 in NMA or PC by precipitation with anhydrous diethyl ether yielded some bulk metal. This important observation means that these

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(45) Creighton, J. A.; Eadon, D. G. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3881.

(46) Umpierre, A. P.; Machado, G.; Fecher, G. H.; Morais, J.; Dupont, J. *Adv. Synth. Catal.* **2005**, *347*, 1404.

(47) Özkar, S.; Finke, R. G. *Coord. Chem. Rev.* **2004**, *248*, 135.

(48) Parks, E. K.; Nieman, G. C.; Kerns, K. P.; Riley, S. J. *J. Chem. Phys.* **1998**, *108*, 3731.

BF_4^-/high-ϵ solvent stabilized, metastable nanoclusters are, however, not sufficiently stable to pass the stringent test of isolability and complete redissolvability without the formation of bulk metal. Nanoclusters prepared under the conditions of Scheme 2 with 1 equiv of BF_4^- present in NMA or PC precipitate out of solution ~5 h after complete nanocluster formation. Additionally, bulk metal was formed during the TTO experiments. These data again indicate that 1 equiv of BF_4^- plus polar solvents provides, at best, metastable transition-metal nanoclusters, at least in the test case of $Ir(0)_n$ nanoclusters.

Increased Solution Stability in PC with 50 or 100 equiv of BF_4^-. We performed three nanocluster formation and stabilization experiments with excess $[Bu_4N][BF_4]$ to increase the amount of BF_4^- over the 1 equiv of BF_4^- present from the reduction of $[(1,5\text{-COD})Ir(CH_3CN)_2][BF_4]$, Scheme 2. While the addition of just a 10-fold excess of $[Bu_4N][BF_4]$ at the beginning of the nanocluster formation reaction had little apparent effect on the solution stability of the resultant nanoclusters in PC, the addition of 50 equiv of $[Bu_4N][BF_4]$ increased the solution stability of the nanoclusters from ~5 h to ≥*2 months* under a N_2 atmosphere. The addition of 100 equiv $[Bu_4N][BF_4]$ gave indistinguishable results vs the 50 equiv $[Bu_4N][BF_4]$ experiment. These results correspond to a ≥288-fold increase in the solution stability. Nanoclusters prepared with 50 equiv of added $[Bu_4N][BF_4]$ are not obviously agglomerated by TEM, but they do show a somewhat broad size distribution of 36 ± 12 Å (see Figure S3 of the Supporting Information). However, despite the increased solution stability of the systems with 50 or 100 equiv of added $[Bu_4N][BF_4]$, neither solution of nanoclusters were isolable or redissolvable.

Reflection upon the improved solution stability and decreased agglomeration with 50 to 100 equiv of added $[Bu_4N][BF_4]$ yields further insights. Normally, added salts result in a *collapse* of the Debye layer[19,22] (recall eq 1, where the concentration of ions in the bulk solution is in the denominator), typically resulting in the precipitation of traditional colloids. This phenomenon is related to the critical coagulation concentration (ccc) concept, described in the literature as a “rather abrupt change from (colloid) stability to instability on changing the salt concentration”.[22] It follows that the *increased stability* seen with 50 to 100 equiv of $[Bu_4N][BF_4]$ demands a different explanation. The obvious one is given in eq 2, in which we hypothesize an equilibrium between the free and surface-bound BF_4^- to account for the increased solution stability with 50 or 100 equiv of $[Bu_4N][BF_4]$. An increase in the concentration of $[Bu_4N][BF_4]$ should shift the equilibrium to the right, which would increase the concentration of surface-bound BF_4^-, thereby providing more DLVO-type anionic (Coulombic repulsion) stability between $[Ir(0)_n{\cdot}(BF_4^-)_x(\text{solvent})_y]^{x-}$ nanoclusters.

$$Ir(0)_n + x[Bu_4N][BF_4] \rightleftharpoons Ir(0)_n{\cdot}(BF_4^-)_x^{x-} + xBu_4N^+ \quad (2)$$

Consistent with more surface-coordinated BF_4^-, the nanoclusters with 50 or 100 equiv of added $[Bu_4N][BF_4]$ proved to be *half* as catalytically active for cyclohexene hydrogenation.

Interestingly, the addition of 480 equiv of $[Bu_4N][BF_4]$, followed by monitoring of the formation reaction in PC, resulted in bulk metal. This is an important finding, one that (i) strongly supports DLVO theory as directly applicable to nanocluster stability since the additional $[Bu_4N][BF_4]$ salt appears to have collapsed the Debye layer consistent with the ccc concept, (ii) documents, therefore, the dual effects of added salt stabilizers, and (iii) means that in the future nanocluster stability needs to be tested as a function of the amount of added salt(s) present.

X-ray Photoelectron Spectroscopy (XPS) of Dried Nanoclusters Prepared with 1 equiv of BF_4^-. The presence of BF_4^- in a film of dried nanoclusters, prepared under the conditions of Scheme 2 in PC, was confirmed by XPS.[49] A high-resolution XPS spectrum showed that ~5% of the total surface composition was attributable to F (see Figure S2 of the Supporting Information), at least in a *solid-state* sample of the (dried) nanoclusters.

Electrophoretic Mobility Experiment Providing Evidence for BF_4^- Coordination in Solution. To provide additional evidence for the coordination of BF_4^- to the $Ir(0)_n$ nanoclusters, we performed an electrophoretic mobility experiment analogous to those we have done before[50] (see Figure S4 for a drawing of the electrophoretic apparatus and see the Experimental Section for details). First, however, a control experiment was done, repeating the electrophoretic mobility demonstrated before for a brown solution of $P_2W_{15}Nb_3O_{62}^{9-}$-stabilized $Ir(0)_n$ nanoclusters (done before, however, in acetone):[50] in PC, a brown band migrated toward the positive electrode, while the solution on the negative side of the apparatus remained clear and colorless, providing good evidence that the proven neutral[50] $Ir(0)_n$ nanocluster core has acquired a net anionic charge by coordinating the 9− polyoxoanion stabilizer.[50] In a separate experiment, a brown solution of $Ir(0)_n$ nanoclusters prepared with 50 equiv of added $[Bu_4N][BF_4]$ also migrated toward the positive electrode, while the solution on the negative electrode side of the apparatus remained clear and colorless. This indicates that the surfaces of the nanoclusters prepared with 50 equiv BF_4^- have an overall negative charge. A separate H_2-uptake experiment confirmed that these specific $Ir(0)_n$ nanoclusters are neutral (as we have demonstrated for the polyoxoanion-stabilized nanoclusters);[50] the H_2 uptake experiment confirmed the stoichiometry in Scheme 2 in which precisely 2.5 equiv of H_2 is taken up per equiv of $[(1,5\text{-COD})Ir(CH_3CN)_2][BF_4]$ so that the resultant $Ir(0)_n$ nanoclusters must be neutral (see the Stabilization by Surface Hydrides section vide infra, for more details). Given that the $Ir(0)_n$ core is neutral, yet the nanoclusters migrate to the

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(49) All of the BF_4^- stability studies were carried out in PC because PC and NMA provided similar results for the 5 criteria as judged by the k_2/k_1 ratio, TEM, and visual observation and because PC is more amenable to work with than NMA (NMA has an inconveniently high melting point of 28 °C and thus frequently crystallizes in syringe needles).

(50) Lin, Y.; Finke, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 8335.

positive electrode of an electrophoretic mobility experiment, and given that BF_4^- is the only anion present, this experiment *confirms that BF_4^- is adsorbed on the nanocluster surface in solution*, $[Ir(0)_n(BF_4^-)_x]^{x-}$. This, in turn, provides further compelling evidence for DLVO-type electrostatic stabilization, in this case with the novel insight that such stabilization is provided by even the traditionally weakly coordinating anion, BF_4^-.

^{19}F NMR Attempts to Detect Coordinated BF_4^-. We used ^{19}F NMR spectroscopy as a direct *solution* method to detect surface-bound BF_4^- on separate nanocluster solutions with either 1 or 50 equiv of BF_4^- present.[51] However, no significant shift in the ^{19}F NMR signal was observed for either nanocluster solution compared to a reference solution of $[Bu_4N][BF_4]$, Figure S5 of the Supporting Information. Recalling our compelling evidence that BF_4^- coordinates to the nanocluster surface (i.e., the increased stability when 1 equiv of BF_4^- is present, the increased stability with 50−100 equiv of BF_4^-, the decreased catalytic activity with increasing BF_4^- equivalents, and the electrophoretic mobility to the positive electrode directly traceable to coordinated BF_4^- as the only anion present), our inability to detect $Ir{\cdot}BF_4^-$ formation by ^{19}F NMR can be rationalized by one or more of the following: (i) we are below the detection limit at the concentrations employed, (ii) there is rapid exchange of the BF_4^- anion, or (iii) there is slow tumbling of the nanoclusters in solution.[52]

Carborane Control Experiment: Further Evidence Supporting BF_4^- as a Nanocluster Surface-Ligating Anion. In light of the negative ^{19}F NMR experiment above, we designed one more experiment to provide additional evidence for (or against) the coordination of traditionally weakly coordinating anions to electrophilic transition-metal nanocluster surfaces. Specifically, we prepared and used the novel organometallic precursor $[(1,5\text{-COD})Ir(CH_3CN)_2][1\text{-}MeCB_{11}F_{11}]$ under the otherwise identical nanocluster synthesis conditions shown in Scheme 2 (see Figure S6 for ^1H, ^{11}B, and ^{19}F NMR spectra and also the Experimental Section for characterazation of this new complex). This nanocluster precursor contains an even more weakly coordinating (than BF_4^-) carborane anion;[53] the resultant nanoclusters should, therefore, be even less stabilized than those with BF_4^-.[54] Indeed, reduction of $[(1,5\text{-COD})Ir(CH_3CN)_2][1\text{-}MeCB_{11}F_{11}]$ under H_2 in PC with 1 equiv PS resulted in a clear colorless solution with bulk metal present (entry 9, Table 2)—that is, the resultant, transient $Ir(0)_n$ nanoclusters were not even metastable. This result provides further confirmation that BF_4^- coordination is an important contribution to $Ir(0)_n$ nanocluster stability and, by implication, to the stability of nanoclusters of other transition-metals in solutions of high ϵ solvents.

Ruling Out Five Alternative Hypotheses for Contributions to Nanocluster Stabilization. We have also considered 5 other (i.e., 7 total) alternative hypotheses for the source of nanocluster stability, such fundamental studies not having been reported before, as well as being necessary to confirm the conclusion of this work that BF_4^- coordination in polar solvents is key to the nanocluster stability.

Stabilization by Trace Chloride. The organometallic precursor $[(1,5\text{-COD})Ir(CH_3CN)_2][BF_4]$ is, ostensibly, halide-free, an important point since Cl^- is an established nanocluster stabilizer.[16,17,55] However, since the above precursor is prepared from the halide-containing dimer, $[(1,5\text{-COD})IrCl]_2$, this leaves open the possibility that trace chloride may be present in the system, the result of a nonstoichiometric reaction with $Ag^+BF_4^-$. Elemental analysis of dried nanoclusters prepared in PC under the conditions of Scheme 2 did, indeed, confirm a trace chloride content of 0.15(2)% (corresponding to 0.008 equiv of Cl^- per Ir). Consequently, an attempt to increase the solution stability of the nanoclusters was made by the addition of Cl^- in the form of additional $[Bu_4N][Cl]$. The addition of up to 1 equiv of $[Bu_4N][Cl]$ per Ir (which allows for >1 Cl^- atom per *surface* Ir atom in the nanoclusters) had no effect on the resultant solution stability of the nanoclusters prepared in PC from $[(1,5\text{-COD})Ir(CH_3CN)_2][BF_4]$; the nanoclusters still precipitated out of solution after ~5 h. Hence, the hypothesis that trace chloride is responsible for the observed solution stability of nanoclusters prepared from $[(1,5\text{-COD})Ir(CH_3CN)_2][BF_4]$ is not supported.

Conceivable Stabilization by Reaction of the Solvent with the Nanocluster Surface. A second alternative hypothesis is that solvents plus reactive nanocluster surfaces could undergo reactions such as the oxidative addition of a C−H bond[56] to form (in this case) surface Ir−R and Ir−H bonds that might serve as steric stabilizers. To test this alternative hypothesis, we carried out the reaction shown in Scheme 2 under both H_2 and D_2 in both PC and NMP. If the solvent reacted with the nanocluster surface (e.g., in a series of oxidative addition and reductive elimination steps), deuterium incorporation is expected. However, GC-MS showed identical elution times and fragmentation patterns under H_2 and D_2 for both PC and NMP; hence, the structure and composition of the solvent appear unchanged. The hypothesis of solvent reaction with the nanocluster surface is, therefore, not supported, the caveat here being that the only reversible reaction[56] would have been detected by our precedented[56] D_2 exchange method.

Stabilization by Surface Hydrides. Under the conditions of relatively high hydrogen pressure that we employ (40 psig), a third alternative hypothesis was that surface hydrides could be formed on the nanoclusters, thereby potentially (sterically?) stabilizing the nanoclusters. Consequently, we performed hydrogen uptake studies in PC in the *absence* of cyclohexene with a sensitive pressure transducer (±0.1 Torr). From Scheme 2, the reaction stoichiometry predicts 2.5 equiv of H_2 should be consumed per 1 equiv of $[(1,5\text{-COD})Ir(CH_3CN)_2][BF_4]$. Experimentally, we observe consumption of 2.6

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(51) For a homogeneous Ir−F complex, the Ir−F bond is observed at −219.3 ppm. Gorol, M.; Mösch-Zaetti, N. C.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-D. *Eur. J. Inorg. Chem.* **2004**, *13*, 2678

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(53) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 133.

(54) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927.

(55) Köhler, J. U.; Bradley, J. S. *Catal. Lett.* **1997**, *45*, 203.

(56) Ott, L. S.; Cline, M. L.; Deetlefs, M.; Seddon, K. R.; Finke, R. G. *J. Am. Chem. Soc.* **2005**, *127*, 5758.

± 0.4 equiv H_2, a result which confirms an analogus finding for polyoxoanion-stabilized $Ir(0)_n$ nanoclusters.[50] Hence, the hypothesis that surface hydrides are a source of the observed solution stability is also not supported.

Possible Stabilization by Scavenged Charge. It has also been shown in the literature that $Pd(0)_n$ nanoclusters are capable of scavenging charge from a W/Al_2O_3 crucible that was part of the reaction apparatus.[12] Consequently, we tested the perhaps remote hypothesis that our $Ir(0)_n$ nanoclusters might also be capable of scavenging charge from the reaction apparatus by performing an electrophoretic mobility experiment analogous to the one described earlier with 50 equiv of $[Bu_4N][BF_4]$ (see the apparatus in Figure S4) on the nanoclusters prepared under the conditions of Scheme 2 with 1 equiv of $[Bu_4N][BF_4]$. The resultant $Ir(0)_n$ nanoclusters were not drawn toward the positive or negative electrode in ~5 h, after which the nanoclusters precipitated out of solution ending the experiment. This experiment indicates that any putative scavenged charge on the nanoclusters is less than that provided by 50 equiv of BF_4^- (which did cause the migration of the nanoclusters, vide supra). In short, this control experiment argues that the formulation of intrinsically anionically charged nanoclusters , "$Ir(0)_n^{x-}$", while conceivable, is an unlikely source of the observed solution stability.

Possible Stabilization by Polymerized Solvent. A fifth alternative hypothesis builds off the plethora of literature examples of nanoclusters stabilized by polymers, including investigations more than 60 years old.[57] While it seems unlikely,[58] it is still conceivable that propylene carbonate could be polymerizing under the reaction conditions to form the known polymer poly(propylene carbonate)[59,60] as a nanocluster stabilizer. Electrospray ionization mass spectrometry (ESI-MS), a technique of demonstrated utility in determining polymeric molecular weights,[61] was employed to test this hypothesis with the finding that no detectable poly(propylene carbonate) is formed under our reaction conditions, Figure S7 of the Supporting Information. Therefore, the hypothesis that $Ir(0)_n$ nanoclusters are stabilized by polymerized PC solvent is also not supported.

In summary, none of the five alternative hypotheses for the source of the solution metastability observed for $[Ir(0)_n{\cdot}(BF_4^-)_x(PC)_y]^{x-}$ nanoclusters in PC are supported. Our prior conclusion that these nanoclusters are stabilized by surface-adsorbed BF_4^- plus PC, along with a Debye multilayer expanded by the polar solvent PC, is therefore further supported.

O_2/Surface Oxide and Pyridine Ligated Nanoclusters: Enhanced Solution Stability. One expects that BF_4^- (weakly) coordinated to nanocluster surfaces should, therefore, be readily replaceable. To test this hypothesis, we exposed a solution of fully formed nanoclusters in PC to oxygen by stirring the nanoclusters under atmospheric O_2 for 15 min.[62] After the nanoclusters prepared under the conditions in Scheme 2 were exposed to oxygen, *the nanoclusters attained enhanced solution stability* (>2 weeks, compared to ~5 h for nanoclusters that had not been exposed to O_2), a ≥67-fold improvement in their solution stability. This experiment is important in at least three respects: (i) it confirms[50,62b] that the as-prepared $Ir(0)_n$ nanoclusters are O_2 sensitive, (ii) it demonstrates that the previously coordinated BF_4^- and solvent are easily displaced by oxidation, and most significantly, (iii) it demonstrates that uncontrolled surface oxygenation of putative solvent-only stabilized nanoclusters may well be a significant source of stability in such literature nanoclusters.

A separate test of the displaceability of the surface ligands of $Ir(0)_n$ nanoclusters prepared with 1 equiv of BF_4^- in PC was performed by addition of the strong ligand pyridine to a solution of the nanoclusters. The solution again attained enhanced solution stability (>2 weeks). This experiment further demonstrates (i) that the BF_4^- and/or PC ligands of $[Ir(0)_n{\cdot}(BF_4^-)_x(PC)_y]^{x-}$ are readily replaced (and thus relatively weakly coordinated), and (ii) that (neutral) strong *ligand* coordination and stabilization is another mode of nanocluster stabilization.[63] As expected, however, the nanocluster solution with added pyridine was catalytically *inactive* toward cyclohexene hydrogenation, indicating pyridine poisoning of the previously catalytically active surface atoms of the nanoclusters.

How Does BF_4^- Compare to the "Gold Standard" $Ir(0)_n$ Nanocluster Stabilizer $P_2W_{15}Nb_3O_{62}^{9-}$? The present "Gold Standard" (poly)anion for nanocluster high stabilization, according to the 5 criteria method and in comparison to 11 anions studied so far,[16,17] is the 9− charged Brønstead basic $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion; this is true even in the lower-ϵ solvent acetone.[16,17,64] As such, the $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion is a valuable reference point for ranking other stabilizers.

Five sets of experiments are reported in the Supporting Information comparing BF_4^- to $P_2W_{15}Nb_3O_{62}^{9-}$ for all five solvents listed in Table 1. The essence of our findings is that $P_2W_{15}Nb_3O_{62}^{9-}$ is a considerably superior stabilizer

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(57) Rampino, L. D.; Nord, F. F. *J. Am. Chem. Soc.* **1941**, *63*, 2745. (b) Rampino, L. D.; Nord, F. F. *J. Am. Chem. Soc.* **1941**, *63*, 3268.

(58) Poly(propylene carbonate) is usually formed by the copolymerization of CO_2 and propylene oxide under the rather harsh reaction conditions (i.e., compared to those of the work reported in the main text) of 50 atm of CO_2, 60 °C, and 40 h in the presence of a metal catalyst.[60]

(59) Chisholm, M. H.; Navarro-Llobet, D.; Zhou, Z. *Macromolecules* **2002**, *35*, 6494.

(60) Zhu, Q.; Meng, Y. Z.; Tjong, S. C.; Zhao, X. S.; Chen, Y. L. *Polym. Int.* **2002**, *51*, 1079.

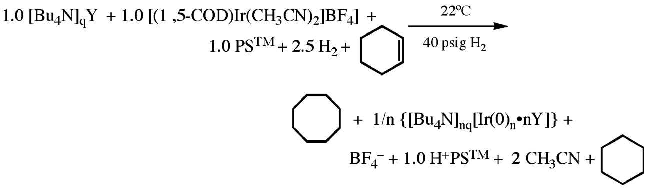
(61) Hanton, S. D. *Chem. Rev.* **2001**, *101*, 527.

(62) Although the oxidation of bulk Ir normally only occurs at high temperatures,[62a] we have recently shown that $Ir(0)_n$ nanoclusters appear to be capable of titrating some contaminant, presumably oxygen, from our ≤5 ppm O_2 drybox.[62b] Consequently, the Ir nanocluster surfaces appear to be more susceptible to oxygenation than bulk metal, as expected for the higher surface area and more energetic nanoclusters (the heat of vaporization of $Ir(0)_n$ to nIr(0) atoms requires 159 kcal/mol,[4] demonstrating the energetic nature of small metal(0) nanoclusters). (a) Cheetham, A. K., Day, P., eds. *Solid State Chemistry Techniques*; Clarendon Press: Oxford, U. K., 1987. (b) Hornstein, B. J.; Finke, R. G. *Chem. Mater.* **2003**, *15*, 899.

(63) Ott, L. S.; Finke, R. G. *Coord. Chem. Rev.* **2006**, in press.

(64) Özkar, S.; Finke, R. G. *Langmuir* **2003**, *19*, 6247.

Scheme 3. Generalized $Ir(0)_n$ Nanocluster Formation Reaction in the Presence of Added Anions, $Bu_4N^+Y^-$,[65] such as $[Bu_4N]_9[P_2W_{15}Nb_3O_{62}]$



compared to BF_4^- in all five solvents under the conditions of 1.2 mM and 22 °C, and as measured by the 5 criteria method.

Further Tests of DLVO Theory: Do Increasingly High-ϵ Solvents Increase the Stability of $Ir(0)_n$ Nanoclusters in the Presence of $P_2W_{15}Nb_3O_{62}^{9-}$? We examined the five solvents shown in Table 1 for the reaction in Scheme 3. A detailed discussion appears in the Supporting Information; the interesting, key result is that the solvent ϵ value *does not appear* to influence the stability of $P_2W_{15}Nb_3O_{62}^{9-}$-stabilized nanoclusters as measured by the 5 criteria. It is not clear at present if this result is a reflection of a breakdown of DLVO theory when non-point-charge, non-unit-charge (poly)anions such as $P_2W_{15}Nb_3O_{62}^{9-}$ are present or an insensitivity of the 5 criteria method. This does, however and therefore, set up $P_2W_{15}Nb_3O_{62}^{9-}$ stabilized nanoclusters in varying ϵ solvents as an important target to restudy if and when an agglomeration kinetic method becomes available for assaying nanocluster stability.

Summary and Conclusions

The highlights of the present work can be summarized as follows.

- Literature claims of solvent-only stabilized nanoclusters are not supported by our findings, at least in the case of $Ir(0)_n$ nanoclusters. Instead and in accordance with DLVO theory, surface-coordinated anions yield repulsive, electrostatic stabilization between nanoclusters.
- Hence, anion coordination and electrostatic stabilization is *the first hypothesis* one should test and support or refute when it comes to claims of how transition-metal nanoclusters are stabilized and prior to postulating unprecedented "solvent-only" or other new stabilization modes.
- Even the traditionally weakly coordinating anions such as BF_4^- *contribute significantly to the stability of prototype $Ir(0)_n$ nanoclusters in high ϵ solvents.* This is a major, previously unappreciated finding.
- Two subhypotheses for the observed nanocluster metastability in the presence of BF_4^- are a possible tridentate facial coordination of BF_4^- on the metal surface[47] and the probability of a particle-size-dependent fractional ligand coverage of the nanocluster surface, with a recently identified up to 2-fold stronger metal−ligand bond dissociation energies in nanoclusters in comparison to the corresponding bulk metal.[25]
- The stability of $[Ir(0)_n{\cdot}(BF_4^-)_x(PC)_y]^{x-}$ nanoclusters is enhanced via the addition of 50−100 equiv of $[Bu_4N][BF_4]$ but is then decreased when larger amounts (480 equiv) of $[Bu_4N][BF_4]$ are added. This was rationalized by the competition of opposing effects: the increase of surface-coordinated of BF_4^- because of the operation of the equilibrium in eq 2 (vide supra) versus the collapse of the Debye layer in accordance with DLVO theory and the concept of a ccc (critical coagulation concentration) salt effect.[19,22]
- Nanocluster stability, then, really makes sense only as function of the amount and specific types of salt and solvent present. Hereafter, each claim and report of nanocluster stability should test the stability *in solution*, as a function of the salt concentration, and in various dielectric constant solvents.
- The solution stability time is improved significantly by exposing the nanoclusters to atmospheric O_2 or pyridine. Hence, the presence or absence of surface oxides needs to be carefully considered and ruled out or supported in each claim of nanocluster stability where the nanoclusters have been exposed to O_2. Nanocluster oxides have received some investigation,[66,67] but deserve systematic study.
- As measured by the 5 criteria, nanoclusters prepared in the presence of 1 equiv of BF_4^- are much less stabilized (and, for example, are not isolable) compared to the highly stabilized isolable nanoclusters with the $P_2W_{15}Nb_3O_{62}^{9-}$ "Gold Standard" (poly)anionic stabilizer.[16] Nevertheless, the findings of weak metastabilization by anions such as BF_4^- in high ϵ solvents may have applications toward solving the naked nanocluster (really, ligand-labile nanocluster)[32] problem.

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(65) In nanocluster formation reactions with added $[Bu_4N]_9[P_2W_{15}Nb_3O_{62}]$, the order of mixing $[Bu_4N]_9[P_2W_{15}Nb_3O_{62}]$ and $[(1,5\text{-COD})Ir(CH_3CN)_2][BF_4]$ has an effect on the nanocluster formation reaction and, hence, the products. It is preferable to make two separate solutions, one containing $[Bu_4N]_9[P_2W_{15}Nb_3O_{62}]$ and one containing $[(1,5\text{-COD})Ir(CH_3CN)_2][BF_4]$ and PS and then to add the solution containing $[(1,5\text{-COD})Ir(CH_3CN)_2][BF_4]$ and PS dropwise to a rapidly stirred solution of $[Bu_4N]_9[P_2W_{15}Nb_3O_{62}]$. This order of addition leads to reproducible kinetics of nanocluster formation, well-fit by the 2-step autocatalytic nanocluster formation mechanism, and to reproducible near-monodisperse $Ir(0)_n$ nanoclusters. This order of mixing, which promotes the formation of a 1:1 metal/polyanion complex, is also corroborated by our earlier work on supported organometallics. For example, see: Pohl, M.; Lyon, D. K.; Mizuno, N.; Nomiya, K.; Finke, R. G. *Inorg. Chem.* **1995**, *34*, 1413 and references therein.

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Experimental Section

Materials and Instrumentation. All commercially obtained reagents were used as received unless otherwise noted. All solvents were stored in the drybox prior to use. *N*-Methylacetamide (Aldrich, 99+%) was purified according to literature procedure.[68] Propylene carbonate (Aldrich, 99.7%) was evacuated under vacuum ($\leq$100 mm of Hg) for at least 4 h and stored over activated 4 Å molecular sieves. Acetonitrile (Aldrich, 99.93+%) and acetone (Burdick and Jackson, 99.9+% by GC) were purged with argon for a minimum of 20 min. Nitromethane (Aldrich, 99+%) was purified according to literature procedures.[69] *N*-Methylpyrrolidinone (Aldrich, 99.5%) was bubbled with Ar for 20 min and stored over activated 4 Å molecular sieves. Cyclohexene (Aldrich, 99%) was freshly distilled over Na metal under argon and stored in the drybox prior to use. Pyridine (Aldrich, 99%) was vacuum distilled and stored over activated 4 Å molecular sieves. CH_2Cl_2 (Aldrich, 99%) was distilled over P_2O_5 and stored in the drybox. The crystalline iridium solvate complex, $[(1,5\text{-COD})Ir(CH_3CN)_2][BF_4]$, was prepared following the procedure for the corresponding hexafluorophosphate salt.[70] The purity of the solvate complex was verified by ^1H NMR (CD_2Cl_2, s (δ 4.3), s (δ 2.6), m (δ 2.3), m (δ 1.8)). Proton Sponge (1,8-bis(dimethylamino)naphthalene, Aldrich, 99%) was stored in the drybox prior to use. The polyoxoanion $[Bu_4N]_9[P_2W_{15}Nb_3O_{62}]$ used in the control reactions was prepared according to our most recent literature procedure.[71] The purity of the polyoxoanion was checked by ^{31}P NMR (CD_3CN, δ −6.5, −13.6 relative to 85% H_3PO_4, plus small impurity peaks at −8.7 and −13.2). $AgBF_4$ (Aldrich, 99%), $[Bu_4N][BF_4]$ (Aldrich, 99%), and C_6F_6 (Aldrich, 99.5+%) were used as received and stored in the drybox.

Gas chromatography was performed using a Hewlett-Packard 5890 Series II GC with a FID detector equipped with a Supelcowax 10 column coupled to a Hewlett-Packard 3395 integrator. Parameters were as follows: $T_1 = 50$ °C, $t_1 = 3$ min, ramp = 10 °C/min, $T_2 = 180$ °C, $t_2 = 14$ min, and injection volume 2 μL. Negative-ion electrospray mass spectrometry (ESI-MS) was performed on a Finnigan LCQ Duo MS directly coupled with a syringe pump. ^1H, ^{11}B, and ^{31}P NMR experiments were carried out on a Varian Inova 300 spectrometer. Spectra were obtained in 5.0 mm o.d. oven dried ($\geq$24 h at 160 °C) NMR tubes at 22 °C in either CD_2Cl_2 or CD_3CN. ^{19}F NMR spectroscopy for this study was carried out using a Varian 400 MHz NMR with the following spectral parameters: acquisition time, 0.599 s; relaxation delay, 4.0 s; sweep width, 34965.0 Hz; scan repetitions, 84. An internal reference of C_6F_6 (set to $\delta = -165.00$) was used. XPS spectra were collected using a Physical Electronics (PHI) Model 5800XPS system equipped with a monochromator (Al Kα source operating at 1486.8 eV; system pressure $\leq 1 \times 10^{-9}$ Torr) and a hemispherical analyzer to detect the ejected electrons.

Hydrogenations. The nanoclusters studied herein were prepared using our "standard conditions".[72,73] Experiments were carried out in an in-house constructed, previously fully described[72,73] hydrogenation apparatus for continuously monitoring the loss of H_2 pressure via an Omega PX621 pressure transducer interfaced to a PC through an Omega D1131 A/D converter. The H_2 gas was purchased in $\leq$99.9% purity (General Air) then passed through O_2 and H_2O scavenger traps (Trigon Technologies). For reactions prepared under the conditions in Scheme 1, 1.7 mg (3.6 μmol) of $[(1,5\text{-COD})Ir(CH_3CN)_2][BF_4]$ was weighed into a 2 dram glass vial. For reactions prepared under the conditions in Schemes 2 and 3, 1 equiv (0.8 mg, 3.6 μmol) of Proton Sponge was also added. For reactions prepared under the conditions in Scheme 3, 22.6 mg (3.6 mmol) of $[Bu_4N]_9[P_2W_{12}Nb_3O_{62}]$ was added.[65] The solvent under study (2.5 mL) was added with a gastight syringe. This solution was mixed with a disposable polyethylene pipet until the solution was homogeneous. Next, the solution was transferred using the pipet to a new 22 × 175 mm Pyrex culture tube with a new 5/8 × 5/16 in. Teflon-coated stir bar. Then, freshly distilled cyclohexene (0.5 mL) was added with a 1.0 mL gastight syringe.

The culture tube containing the reaction solution was then placed in a Fischer−Porter (F−P) bottle. The F−P bottle was sealed and brought out of the drybox. Next, the F−P bottle was placed in a jacketed reaction flask with temperature control at 22.0 ± 0.1 °C by means of a constant-temperature circulating water bath. The F−P bottle was attached to the hydrogenation apparatus with Swagelok TFE-sealed Quick-Connects. The stirring was initiated at $\geq$600 rpm,[74] and the F−P bottle was purged 13 times (once every 15 s for a total of 3 min and 15 s) with 40 ± 1 psig H_2 gas. After five minutes, $t = 0$ was set, and data collection began. Pressure uptake data was fitted to the analytical form for autocatalysis[43] using ORIGIN 7.0. Formation of the nanoclusters was monitored directly by the evolution of cyclooctane by GLC as previously documented.[43]

Catalytic Activity, Nanocluster Isolation, and Redispersability Experiments. After the minimum time required for the complete formation of nanoclusters, as judged by a separate cyclooctane evolution experiment,[43] the F−P bottle was disconnected, vented, sealed, and brought into the drybox. Three aliquots of the reaction solution (0.5 mL each) were removed from the culture tube using a 1.0 mL gastight syringe. The first aliquot was placed in a new culture tube with a new stir bar and diluted to 2.5 mL with the solvent under study. Next, freshly distilled cyclohexene (0.5 mL) was added to the culture tube with a 1.0 mL gastight syringe. Last, the culture tube was sealed in the F−P bottle, brought out of the drybox, and hydrogenation was initiated as described herein.

The other two 0.5 mL aliquots taken were used for transmission electron microscopy (TEM) analysis (see Transmission Electron Microscopy section below) and nanocluster redispersability experiments. Neither NMA nor PC is sufficiently volatile to allow for simple solvent removal under vacuum (NMA boils at ∼204−206 °C; PC at 240 °C). Accordingly, nanoclusters prepared in these solvents were precipitated with diethyl ether with a procedure established elsewhere.[75] The isolated nanoclusters were then redispersed by addition of the solvent under study (2.5 mL) to the dried nanocluster film followed by aggitation with a polyethylene pipet until the solution was a homogeneous light brown (NB, this was only possible for $P_2W_{15}Nb_3O_{62}^{9-}$-stabilized nanoclusters, as none of the nanoclusters prepared with BF_4^- were completely redispersable without the formation of bulk metal). Using the polyethylene pipet, the redispersed nanocluster solution was transferred into a new culture tube with a new stir bar, and freshly distilled cyclohexene (0.5 mL) was added. The culture tube was placed in the F−P bottle, which was subsequently sealed, removed from the drybox, and attached to the hydrogenation apparatus. Hydrogenation was initiated exactly as described in the Hydrogenations section.

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Transmission Electron Microscopy (TEM). TEM analysis was carried out with the expert assistance of Dr. JoAn Hudson first at the University of Oregon, then later at Clemson University. As described previously,[16] micrographs at Oregon were obtained with a Phillips CM-12 microscope operating at 100 keV. Micrographs at Clemson were obtained using a Hitachi H7600T operating at 120 kV. Size measurements were obtained from micrographs with 430 000 magnification or higher. Size distributions of nanoclusters were determined by counting >100 nanoclusters. Since propylene carbonate is not a suitable solvent for preparing TEM grids,[75] if they are prepared by a "standard" method (i.e., if they are prepared by placing two drops of the diluted reaction solution onto TEM grids), the reaction solutions were instead sprayed onto TEM grids using an asthmatic's nebulizer (PulmoAide, model 5610D). In the drybox, the reaction solution (0.5 mL) was syringed into a new disposable medicine cup; 300 mesh silicon monoxide TEM grids (Ted Pella, Inc.) were carefully held with tweezers in front of the nebulizer mouthpiece while the reaction solution was nebulized. After trials with 5, 10, 15, and 30 s of nebulization time, it was determined that 5 s exposure time was sufficient to visualize the nanoclusters. Control TEM images of $P_2W_{15}Nb_3O_{62}{}^{9-}$−stabilized $Ir(0)_n$ nanoclusters in acetone, prepared either by the "standard" dried droplet method, or the nebulizer method confirmed that both techniques yield statistically indistinguishable results. Dark-field TEM images were inverted and then enlarged using Adobe Photoshop 7.0.

Total Turnover (TTO) Experiments. The total turnover experiments were carried out exactly as reported previously.[16,17]

XPS of Dried Nanoclusters Prepared with 50 equiv of Added $[Bu_4N][BF_4]$. A nanocluster formation reaction was carried out exactly as described in the Hydrogenations section. Then, the nanoclusters were precipitated from solution in a scintillation vial following our literature procedure.[75] In the drybox, the scintillation vial was broken with a hammer. A portion of the vial with metal, visible to the naked eye, plated out on it was sealed in a separate oven-dried glass scintillation vial, which was subsequently sealed with electrical tape. The vial was removed from the drybox. Then, under flowing N_2, a portion of the metal-coated vial was mounted onto a XPS sample holder with Scotch tape. After the sample chamber was thoroughly evacuated ($\leq 10^{-9}$ Torr), sample analysis was initiated.

Hydrogenations with Excess $[Bu_4N][BF_4]$. These experiments were carried out as described in the Hydrogenations section with the following modification: to the glass vial containing $[(1,5\text{-COD})Ir(CH_3CN)_2][BF_4]$ and PS, 10, 50, or 100 equiv of $[Bu_4N][BF_4]$ (36, 180, or 360 μmol) were added. The rest of the hydrogenation procedure was carried out exactly as reported.

Electrophoretic Mobility Experiments. The apparatus used herein was a modification of a previously used[50] glass U-tube with an addition arm. For the experiments herein, a glass tube in a W shape with an addition arm and two fine glass frits was used (see Figure S4 in the Supporting Information). An electrolyte solution (40 mL) of 2 mM $[Bu_4N][BF_4]$ in PC was prepared and used to fill both arms of the W-tube. Then, a solution of fully formed nanoclusters in PC was added to the addition arm with the stopcock closed. Two Pt wire electrodes were immersed in the electrolyte solution in the arms of the W-tube. After the stopcock was opened and the nanocluster solution was allowed into the center of the W-tube, a voltage of 21 V was applied with a Keithley 2400 SourceMeter. An analogous experiment was carried out with nanoclusters prepared under the conditions of Scheme 1 but with 50 equiv of added $[Bu_4N][[BF_4]$. Two control experiments, with either $P_2W_{15}Nb_3O_{62}{}^{9-}$- or Cl-stabilized nanoclusters, were also performed to confirm the expected migration of the known (in the case of $P_2W_{15}Nb_3O_{62}{}^{9-}$)[50] negatively charged nanoclusters toward the positive electrode.

^{19}F NMR Spectroscopy. As a control to establish the spectrum of free BF_4^-, $[Bu_4N][BF_4]$ (1.0 mg, 3.0 μmol) was dissolved in propylene carbonate (0.75 mL) with two drops C_6F_6. An aliquot of this solution (100 μL) was dissolved in CD_2Cl_2 for analysis. For the two reaction solutions, 100 μL of either a nanocluster solution prepared under the conditions of Scheme 1 or a nanocluster solution with 50 equiv of added $[Bu_4N][BF_4]$ was diluted in 0.5 mL of CD_2Cl_2 with two drops C_6F_6.

Preparation of the Carborane Complex $[(1,5\text{-COD})Ir(CH_3CN)_2][1\text{-Me-}CB_{11}F_{11}]$. The carborane solvate complex was prepared by a modification of literature procedures.[70] All glassware used was oven-dried for ≥ 12 h at 160 °C. In a 25 mL Erlenmeyer flask, freshly prepared[76] $Cs[1\text{-Me-}CB_{11}F_{11}]$ (51.1 mg, 0.105 mmol) was dissolved in 10 mL of CH_2Cl_2. $AgBF_4$ (20.4 mg, 0.105 mmol) was added to the carborane solution, precipitating $CsBF_4$ as a white powder. The solution was gravity filtered through a Whatman no. 2 filter, yielding a clear colorless $Ag[1\text{-Me-}CB_{11}F_{11}]$ solution. Separately, in a 25 mL Erlenmeyer flask, $[(1,5\text{-COD})IrCl]_2$ (35.6 mg, 0.053 mmol) was dissolved in ∼10 mL of CH_2Cl_2 with stirring, yielding a clear bright-red solution. Next, CH_3CN (1.0 mL) was added with a gastight syringe to the $[(1,5\text{-COD})IrCl]_2$ solution, immediately producing a clear bright-yellow solution. Then, the Ir solution was added to the $Ag[1\text{-Me-}CB_{11}F_{11}]$ solution with a polyethylene pipet. This addition yielded a bright-yellow solution and precipitated, white AgCl. The solution was gravity filtered through a Whatman no. 2 filter into a 50 mL Erlenmeyer flask which contained ∼10 mL of anhydrous diethyl ether. The flask was covered with a KimWipe, and the solvent was allowed to slowly evaporate over a period of 3 days. $[(1,5\text{-COD})Ir(CH_3CN)_2][1\text{-Me-}CB_{11}F_{11}]$ (45.3 mg, 58% yield) was collected as a brilliant-yellow powder and characterized by ^{1}H, ^{11}B, and ^{19}F NMR spectroscopy (Figure S4 in the Supporting Information). ^{1}H NMR: s (δ 4.3), s (δ 2.6), s (δ 2.3), m (δ 2.0), m (δ 1.8), s (δ 1.6), m (δ 1.3), corresponding to the expected proton peaks for the Ir solvate complex (vide infra) plus the protons from the carborane methyl group. ^{11}B NMR spectroscopy showed two broad peaks centered at $\delta = -10$ and -18, corresponding to the terminal and belt boron atoms of the icosahedral carborane, respectively. Boron-decoupled ^{19}F NMR spectroscopy showed the peaks at s (δ −253), s (δ −258), and s (δ −260), corresponding to the terminal fluorine atom and the two belts of fluorine atoms, respectively. Literature ^{11}B and ^{19}F NMR spectra for the $Cs[1\text{-Me-}CB_{11}F_{11}]$ complex are available.[76]

Nanocluster Formation under H_2 and D_2 for GC-MS. These experiments were carried out exactly as described in the Hydrogenations section with the exception that D_2 was substituted for H_2 in two of the reactions. The D_2 gas (matheson Tri-Gas; 99.5%) was used as received. After complete nanocluster formation, the F−P bottle was vented, sealed, and brought into the drybox. Aliquots (0.5 mL) of each of the four reaction solutions were placed into predried 1.0 mL GC vials and capped with PTFE-lined crimp top caps. Prior to ESI-MS, the solutions were diluted 10-fold in CH_3CN.

Elemental Analysis. The nanocluster material was isolated from PC by precipitation with diethyl ether following a literature procedure.[75] The samples were sealed under nitrogen, double-bottled, and sent to Galbraith Laboratories for analysis (Knoxville, TN). The Cl^- content of the samples was determined by ICP.

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Hydrogen Uptake Experiment. The hydrogen uptake was monitored using the same apparatus and technique previously described.[44] Briefly, in a nitrogen-atmosphere drybox, $[(1,5\text{-COD})\text{Ir}(CH_3CN)_2][BF_4]$ (10.1 mg, 21.5 μmol) was weighed into a predried 2 dram glass vial, and propylene carbonate (5 mL) was added with a 10.0 mL gastight syringe. This bright-yellow solution was agitated with a disposable polyethylene pipet until the solution was homogeneous and transferred into a predried 50 mL Pyrex reaction bulb which contained a 1 × 3 mm Teflon-coated stir bar. The 2 dram vial was rinsed with an additional 5 mL of PC, and the rinse solution was also added to the reaction bulb. A final 5 mL of PC was added, bringing the final reaction volume to 15 mL. The reaction bulb was sealed, brought out of the drybox, and attached to the vacuum line apparatus as shown in Figure A of the Supporting Information elsewhere.[44] The solution was degassed via three freeze−pump−thaw cycles and then vortex stirred for ≥1 h to attain a stable temperature. With the reaction flask isolated and under vacuum, the manifold was pressurized to ∼640 Torr with H_2 (approximately 1 atm pressure at our mile-high altitude). Next, the reaction flask was opened to the manifold, $t = 0$ was set, and an initial pressure was noted. Pressure was monitored every 5 min with an MKS Baratron Pressure Gauge.

ESI-MS. Nanoclusters were prepared in PC as described in the Hydrogenations section. Samples were prepared by diluting 1 μL of the reaction solution or control solution in 1 mL of 50/50 MeOH/H_2O.

Exposure of Fully Formed Nanoclusters to Oxygen or the Strong Ligand Pyridine. (*a*) *O_2*. After complete nanocluster formation, as judged by a separate cyclooctane evolution experiment, the F−P bottle was disconnected from the hydrogenation apparatus and opened outside the drybox. The dark-brown nanocluster solution was stirred for 15 min. Then, the nanocluster solution was decanted into a predried glass scintillation vial which was first evacuated and then placed in the drybox. (*b*) *Pyridine*. After complete nanocluster formation, as judged by a separate cyclooctane evolution experiment,[43] the F−P bottle was disconnected from the hydrogenation apparatus, vented, sealed, and brought into the drybox. With a polyethylene pipet, the dark-brown nanocluster solution was transferred into a predried glass scintillation vial containing a Teflon-coated magnetic stir bar. Pyridine (1 mL, 12.4 mmol, ∼3000 equiv vs Ir) was added to the scintillation vial with a gastight syringe with stirring. Then, the nanocluster solution was vortex stirred for 15 min to ensure complete mixing of the pyridine. The nanocluster solution was kept sealed in the drybox while the solution stability was monitored.

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Supporting Information Available: Table S1, the solvent-only stabilized nanocluster literature; Figure S1, possible reaction of nitromethane with Proton Sponge; a discussion of stabilization by BF_4^- in low-ϵ solvents plus a structural comparison of NMP and poly(vinylpyrrolidone); Figure S2, XPS spectrum of dried nanoclusters prepared under the conditions of Scheme 1; Figure S3, TEM image of nanoclusters prepared with 50 equiv of added $[Bu_4N][BF_4]$; Figure S4, cartoon of the apparatus for the electrophoretic mechanism experiment; Figure S5, ^{19}F NMR spectra investigating the coordination of BF_4^-; Figure S6, ^1H, ^{11}B, and ^{19}F NMR spectra of $[(1,5\text{-COD})\text{Ir}(CH_3CN)_2][1\text{-Me-CB}_{11}F_{11}]$; Figure S7, ESI-MS spectra of neat PC and of the reaction solution in PC; Figure S8, the difference in kinetic control[77] of the nanocluster formation reaction in propylene carbonate for nanoclusters prepared with and without added $P_2W_{15}Nb_3O_{62}^{9-}$; and a discussion of $P_2W_{15}Nb_3O_{62}^{9-}$-stabilized $\text{Ir}(0)_n$ nanocluster stability in solvents of varying ϵ. This material is available free of charge via the Internet at http://pubs.acs.org.

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(77) Formation and stabilization of nanoclusters are tightly interlinked issues as has been illustrated for Pt(0) nanoclusters.[25] Also see: Besson, C.; Finney, E. E.; Finke, R. G. *Chem. Mater.* **2005**, *17*, 4925.