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Communication

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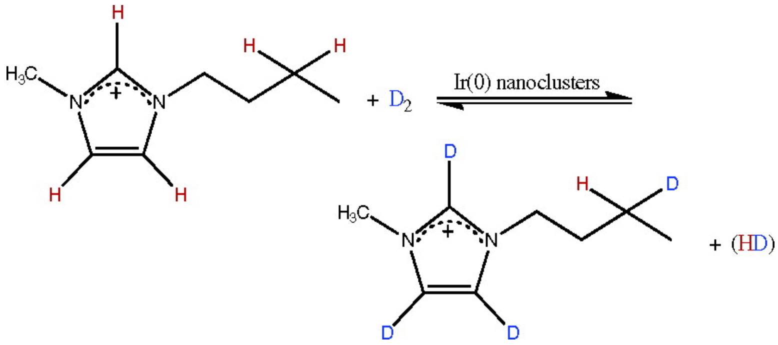

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COMMUNICATIONS

Nanoclusters in Ionic Liquids: Evidence for *N*-Heterocyclic Carbene Formation from Imidazolium-Based Ionic Liquids Detected by ^{2}H NMR

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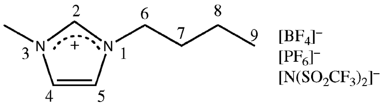
Ionic liquids (ILs) are very good *apparent* stabilizers of transition-metal nanoclusters/nanocolloids.[1−7] However, *precisely how* ILs stabilize transition-metal nanoclusters has remained a mystery since only nonbasic anions, such as $[BF_4]^-$, $[PF_6]^-$, or $[N(SO_2CF_3)_2]^-$, Scheme 1, are typically present, albeit in high concentrations in neat ILs. Can even such weakly coordinating anions bind tightly to nanocluster surfaces to provide classic, anion-based, DLVO (Dergaugin−Landau−Verwey−Overbeek)-type Coulombic repulsion between, and thus stabilization of, (nano)colloidal particles?[8] Or, is there some other source of nanocluster stabilization in ILs?

Scheme 1. Three 1-Butyl-3-methylimidazolium ($[bmim]^+$)-Based ILs Utilized in the Present Studies. The $[N(SO_2CF_3)_2]^-$ Anion is Abbreviated herein, as in the Literature, as $[NTf_2]^-$

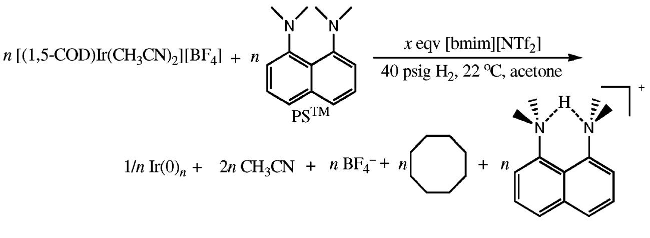


Herein, after confirming that ILs provide high nanocluster stabilization in our hands as in the literature, we tested five alternative hypotheses as to the source(s) of this high stabilization. Our results (i) provide compelling D labeling and ^{2}H NMR evidence for *the formation of N-heterocyclic carbenes from imidazolium-based ILs*; (ii) provide, thereby, the first evidence for N-heterocyclic carbene ligation of a nanocluster; (iii) contribute to the growing literature implicating some ILs as noninnocent solvents;[9−13] and (iv) illustrate an easily implemented ^{2}H NMR-based technique[14] for the detection of H/D exchange reactions on reactive nanocluster surfaces. The latter is significant in its own right since nanoclusters hold considerable potential to serve as well defined, easily studied, soluble analogues of the commercially important heterogeneous catalysts.[15]

We chose the $Ir(0)_n$ nanoclusters in Scheme 2 for our studies based on prior work[15−17] which rates the relative efficacy of transition-metal nanocluster stabilizers using $Ir(0)_n$ as a prototype system.[17] Scheme 2 illustrates the synthesis of the $Ir(0)_n$ nanoclusters via the reduction of $[(1,5\text{-COD})Ir(CH_3CN)_2]BF_4$ (**1**) under H_2 in the presence of Proton Sponge (PS) *in acetone*, with predetermined but variable amounts (x equiv, Scheme 2) of $[bmim][NTf_2]$ present.

First, control experiments were performed to confirm that the IL is the source of a high degree of stabilization of the Ir(0) nanoclusters. With *no* added IL, a colorless, clear reaction solution plus bulk metal (only) results. However, increasing the $[bmim][NTf_2]$ to 10 equiv yields a stable, dark-brown Ir(0) nanocluster[18] solution (no bulk metal was observed) containing 2.1 ± 0.6 nm nanoclusters by transmission electron microscopy (TEM; 201 particles counted). A TEM control consisting of the precursor alone in the IL did not yield nanoclusters; that is, the observed nanoclusters are not an artifact of precursor reduction in the energetic TEM beam.[19] With higher (100, 250, and 480) equiv of IL (the latter equaling neat $[bmim][NTf_2]$), stable, dark-brown nanocluster solutions are formed that are stable against agglomeration for >1 year. Ir(0) nanoclusters in $[bmim][NTf_2]$ IL are, therefore, highly stabilized.

Scheme 2. $Ir(0)_n$ Nanocluster System Employed Herein



Next, we experimentally excluded trace Cl^-, H_2O, or coordination by CH_3CN or Proton Sponge as sources of the observed high stabilization (see the Supporting Information for details). We were forced, therefore, to the alternative hypothesis that the *cationic*, imidazolium component of ILs might, surprisingly and unprecedentedly, be interacting or reacting with the nanocluster surface by either: (i) a little precedented, seemingly unlikely, but conceivable,[20] η^5-coordination of the imidazolium *cation* to the *electron-deficient* metal(0) surface; or more likely by (ii) C−H oxidative addition of the acidic, aqueous $pK_a \approx 24$ C−H bond[21] in the 2-H position of the imidazolium cation, resulting in N-heterocyclic carbene formation atop the nanocluster's metal(0) surface.

The crucial experiments detecting surface-ligand-coordinated N-heterocyclic carbene formation in ILs were accomplished using D_2 plus ^{2}H NMR spectroscopy (Figure 1). *Deuterium incorporation is apparent at the 2-H, 4-H, 5-H, and 8-H positions of the imidazolium cation*. ^{1}H NMR spectra of the same reaction solution confirmed the expected decreased intensity of the 2-, 4-, 5-, and 8-H hydrogens in the $[bmim][NTf_2]$ (see Table S3 of the Supporting Information). A control experiment shows that if the nanocluster precursor **1** is omitted from the reaction, no D incorporation into the imidazolium cation occurs; this rules out carbene formation by base deprotonation of the weak, (aqueous) $pK_a \approx 24$ imidazolium acid 2-H site[22−28] by the (aqueous) $pK_a \approx 12.4$ base Proton Sponge, $\Delta pK_a = 11.6$.

Instead, a sequence of N-heterocyclic carbene formation by oxidative addition[29,30] of the imidazolium cation, H/D scrambling atop the nanocluster surface, then reductive elimination of a C−D bond is implicated. However, since precedent exits for the oxidative addition of imidazolium salts to iridium organometallic complexes,[31,32] the kinetics of deuterium incorporation as a function of time were studied to distinguish the nanocluster versus iridium organometallic complex H/D exchange mechanisms. If the Ir(0) nanoclusters are the true catalyst (i.e., and must be formed before H/D exchange can occur), then an induction period plus sigmoidal, autocatalytic kinetics diagnostic of nanocluster formation[33,34] should

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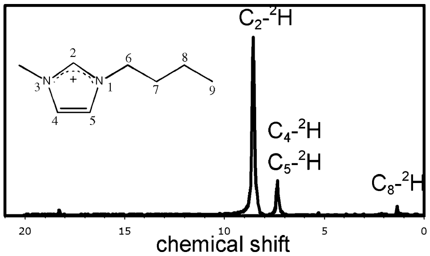

Figure 1. ^{2}H NMR spectroscopy showing deuterium incorporation in the 2-, 4-, 5-, and 8-positions of the imidazolium cation, [bmim]$^+$. The rate of D incorporation is faster for the 2-, 4-, and 5-positions; incorporation at the 8-position of the alkyl chain is slower (>8 h), as discussed in the Supporting Information.

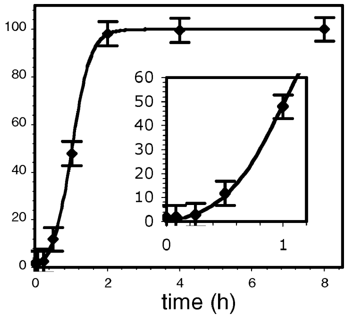

Figure 2. Deuterium incorporation kinetics into the 2-H position of [bmim]$^+$. The curve fit is to the A → B (rate constant k_1), then A + B → 2B (rate constant k_2) mechanism diagnostic of transition-metal nanocluster nucleation and autocatalytic surface growth.[33,34] The data were fit with MacKinetics, yielding the rate constants $k_1 = 0.078(6)$ and $k_2 = 0.038(3)$.

be observed, A → B, then A + B → 2B. On the other hand, if **1** is the key H/D exchange catalyst, then *no induction period* and smooth, presumably second-order kinetics should be observed.

Figure 2 shows the results of eight separate, time-dependent NMR experiments (one for each data point shown), under D_2 with 3.6 mM (10 equiv) of [bmim][NTf$_2$] in acetone at 22 °C. As predicted for the nanocluster as the true H/D exchange catalyst, deuterium incorporation in the 2-H and 4-H (Figure S1) positions occurs *only after an induction period*. Moreover, the kinetics are well-fit by the analytic equations corresponding to the A → B, plus A + B → 2B mechanism diagnostic of nanocluster formation, Figure 2. The coordinatively unsaturated surface of the nanocluster is clearly implicated as the true catalyst.

In conclusion, Ir(0) nanoclusters react with imidazolium-based ILs to form surface-attached carbenes, at least transiently. This contributes to the growing literature implicating some ILs as noninnocent solvents[9−13] and raises a new hypothesis, *carbene-ligand-stabilized* nanoclusters, as to how imidazolium-based ILs could be providing some stabilization to transition-metal nanoclusters.[1,36] The present studies also provide the first example of a carbene ligating a nanocluster surface, and suggest that N-heterocyclic carbene ligation and stabilization of nanoclusters is a topic which merits further investigation. Note that some π bound, η^5-imidazolium cation atop the nanocluster surface is still conceivable, although there is presently no evidence for it. In addition, DLVO-type stabilization by coordination of even anions such as [BF$_4$]$^-$, [PF$_6$]$^-$ or [N(SO$_2$CF$_3$)$_2$]$^-$ to electron-deficient nanocluster surfaces under neat IL (i.e., high concentration, no co-solvent) conditions is still possible if not probable in our opinion.

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Supporting Information Available: Additional materials referred to in the text, as well as additional experiments (e.g., in neat IL), data, evidence, discussion, and additional references (30 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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