Inorganic Chemistry
Communication

Inorg. Chem. **2011**, *50*, 717–719 **717**
DOI: 10.1021/ic102041q

Enhanced Rate of Arene Hydrogenation with Imidazolium Functionalized Bipyridine Stabilized Rhodium Nanoparticle Catalysts

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Received October 8, 2010

The imidazolium functionalized bipyridine compounds, {4,4′-bis-[7-(2,3-dimethylimidazolium)heptyl]-2,2′-bipyridine}$^{2+}$ ([BIHB]$^{2+}$) and {4,4′-bis[(1,2-dimethylimidazolium)methyl]-2,2′-bipyridine}$^{2+}$ ([BIMB]$^{2+}$), were prepared and used as Rh nanoparticle stabilizers. The dispersed Rh nanoparticles were used as catalysts in the biphasic hydrogenation of various arene substrates. The catalytic activity was strongly influenced by the stabilizer employed and followed the trend [BIHB]$^{2+}$ > bipy > [BIMB]$^{2+}$. The steric and electronic characteristics of the imidazolium functionalized bipyridine ligands were assessed via the synthesis of rhenium carbonyl complexes, which facilitated the rationalization of the catalytic properties of the nanoparticles.

Soluble metal nanoparticle (NP) catalysts show considerable promise in arene hydrogenation reactions, demonstrating both high activity and high stability.[1] Since "naked" NPs are inherently unstable, protective agents are generally employed to prevent agglomeration.[2] In this respect, ionic liquids (ILs) appear to act as stabilizers, preventing NP agglomeration, although the use of ILs in combination with additional stabilizers can enhance catalysis and help prevent the formation of bulk metal particles.[1c] Examples of stabilizers used to enhance NP stability during catalytic hydrogenations include ligands,[4] polymers,[1a] solid supports,[8] and functionalized ILs.[9] Of note, N-vinylpyrrolidone (NVP) copolymerized with various vinyl imidazolium derivatives was used to stabilize Rh NPs in ILs that were subsequently used to catalyze biphasic arene hydrogenation reactions.[1a] An imidazolium functionalized dipyridylamine compound has also been used in IL biphasic Pd NP olefin hydrogenations.[9] It was found that the introduction of the imidazolium functionalized stabilizers resulted in superior activity and stability of the NP systems, offering a versatile strategy for the development of NP stabilizers applied in ILs. Indeed, traditional homogeneous catalysts used in ILs also benefit from the incorporation of imidazolium groups onto the ligands coordinated to the catalysts.[10]

Initial work using ligands in the synthesis of NPs in ILs employed phenanthroline to stabilize Pd NP catalysts in olefin hydrogenations.[11] Bipyridine (bipy) based ligands have also been employed in the synthesis of NPs used to catalyze

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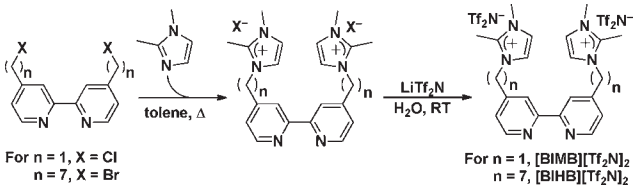
Published on Web 01/05/2011

Scheme 1. Synthesis of $[BIMB][Tf_2N]_2$ and $[BIHB][Tf_2N]_2$



hydrogenations under biphasic conditions.[4] Olivier-Bourbigou and co-workers have also shown that the catalytic activity of bipy stabilized Rh NPs can be tuned by altering the structure of the bipyridine ligand, including derivatization with an imidazolium functionality. Moreover, these Rh NPs tended to agglomerate under catalytic conditions in the absence of stabilizers, emphasizing the importance of stabilizers for NPs immobilized in ILs, which are stable against hydrogenation under catalytic conditions.

Herein, the synthesis of two new imidazolium functionalized bipy ligands and their application as NP catalyst stabilizers is described and correlated to the steric and electronic effects of the modified ligands. It is shown that functionalization increases both the activity of the NP catalysts in arene hydrogenation and retention of the NPs in the reaction medium during product extraction.

Two imidazolium-functionalized bipy stabilizers, {4,4′-bis[7-(2,3-dimethylimidazolium)heptyl]-2,2′-bipyridine}$^{2+}$ ($[BIHB]^{2+}$) and {4,4′-bis[(1,2-dimethylimidazolium)methyl]-2,2′-bipyridine}$^{2+}$ ($[BIMB]^{2+}$), were prepared according to the route shown in Scheme 1. The halogenated intermediates were synthesized using literature methods,[12,13] with the imidazolium functionality introduced by reacting the halogenated intermediate with an excess of 1,2-dimethylimidazole. The halide ions present in $[BIHB]Br_2$ and $[BIMB]Cl_2$ were exchanged for Tf_2N^-, since this anion has been shown to be ideal in NP catalysis, endowing the NPs with stability while also providing good activity.[1c,14] NMR spectroscopy and electrospray ionization mass spectrometry corroborate the expected structures of the ligands (see the Supporting Information) as well as negative silver halide tests confirming complete halide removal during metathesis.

Rh NPs stabilized by $[BIHB][Tf_2N]_2$, $[BIMB][Tf_2N]_2$, or bipy (used as a control) were prepared using a commonly employed approach. Rhodium chloride was dissolved in THF and 1-butyl-3-methyl-imidazolium 1,1,1-trifluoro-N-[(trifluoromethyl)sulfonyl]methanesulfonamide ([bmim]-$[Tf_2N]$) and reduced to Rh(0) by the addition of $NaBH_4$ dissolved in a minimal amount of water. The appropriate ligand was then added as a THF solution (see the Supporting Information for further details). The Rh NPs were characterized by TEM, with their presence verified by an X-ray scattering experiment (see the Supporting Information), revealing that the three stabilizers give rise to NPs with a size distribution centered around 2 nm, with the majority of the particles between 1 and 3 nm (Figure 1). NMR analysis of the catalyst solutions indicated that only trace amounts of the ligand were free in solution, with the rest coordinated to the NP surface (see the Supporting Information).

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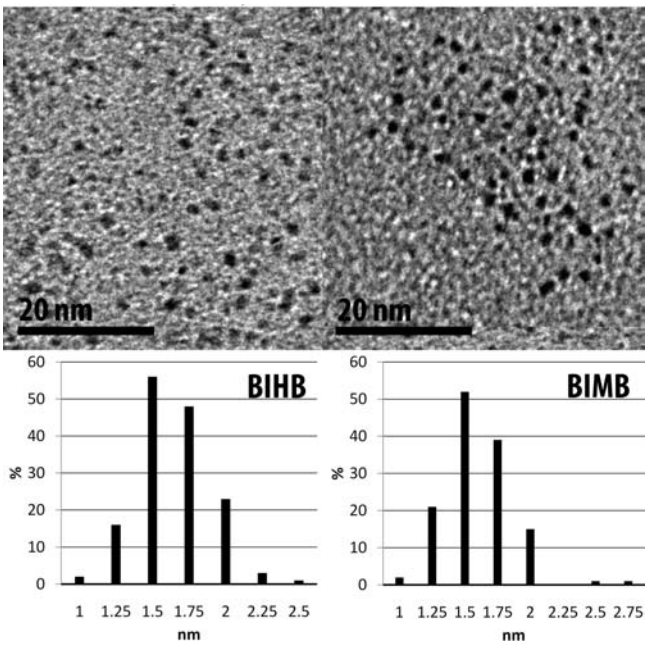

Figure 1. TEM images and size distribution of the Rh NPs stabilized by $[BIHB][Tf_2N]_2$ (left) and $[BIMB][Tf_2N]_2$ (right).

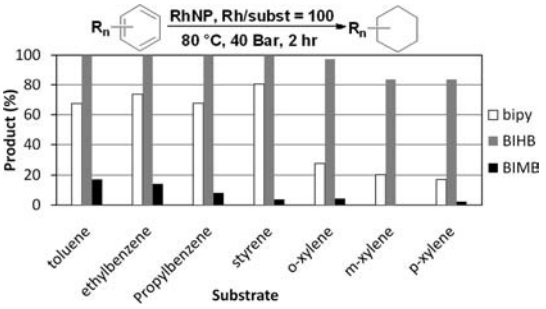

Figure 2. Percent of the hydrogenated product obtained in the Rh NP catalyzed hydrogenation of various substrates using bipy (white), $[BIHB][Tf_2N]_2$ (gray), or $[BIMB][Tf_2N]_2$ (black) stabilizers. Reaction conditions: Rh (0.019 mmol), ligand (0.0095 mmol), subst/Rh = 100, 80 °C, 40 bar H_2, 6 h.

The Rh NPs were evaluated as catalysts for the hydrogenation of aromatic substrates using conditions similar to those described previously (Figure 2).[4d] The nature of the NP stabilizer significantly influences catalytic activity. NPs stabilized by $[BIHB][Tf_2N]_2$, with a C_7 alkyl chain separating the imidazolium functionality from the pyridine backbone, are considerably more active than the bipy-stabilized system (with increases in conversion by as much as 68% observed). The NPs protected by the $[BIMB][Tf_2N]_2$ stabilizer, with one CH_2 group between the imidazolium and the pyridine, result in the lowest activity (Figure 2).

All three catalyst solutions were recycled three times without an appreciable loss of activity. Furthermore, the catalytic systems based on bipy and $[BIHB][Tf_2N]_2$ were active at a reduced temperature (conversions of 51 and 78%, respectively, at 35 °C, 40 bar H_2, toluene/Rh ratio of 990:1, 22 h reaction time).

The lower activity of the $[BIMB][Tf_2N]_2$ stabilized NPs may result from the weaker interaction of the ligand with the metal surface due to the electron withdrawing effect of the imidazolium cation, the greater steric bulk, and the close proximity of the positive charges to the NP surface that,

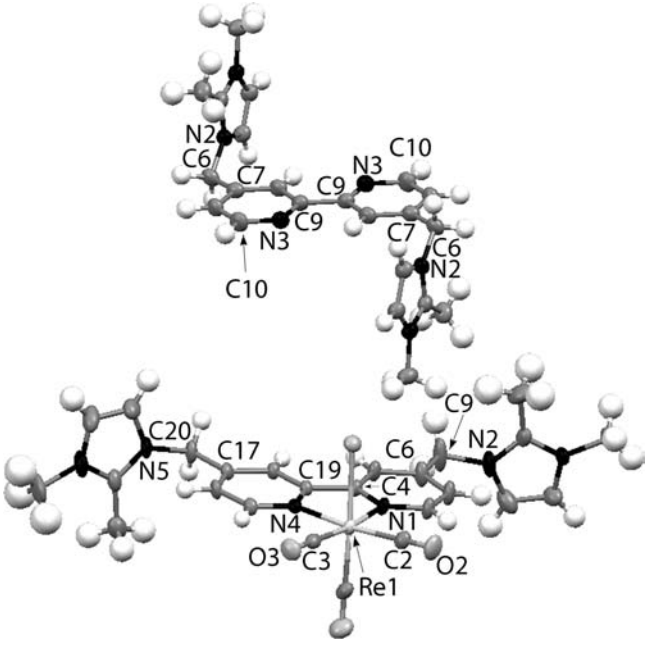

Figure 3. Molecular structures of (top) $[BIMB]Cl_2 \cdot (H_2O)_{0.5}$ and (bottom) $[ReCl(BIMB)(CO)_3][Tf_2N]_2$ represented with ellipsoids at 50% probability. The counteranions and solvate have been omitted for clarity. Selected distances (Å) and angles (deg) (top) N(3)−C(9) 1.363(4), N(3)−C(10) 1.342(5), C(10)−N(3)−C(9) 116.8(3), N(2)−C(6)−C(7) 113.7(3), N(3)−C(9)−C(9) 115.9(4); (bottom) Re(1)−C(2) 1.908(6), Re(1)−C(3) 1.929(5), Re(1)−N(1) 2.155(4), Re(1)−N(4) 2.170(4), N(4)−C(19) 1.358(6), N(1)−C(4) 1.351(6), C(2)−Re(1)−C(3) 86.6(2), N(1)−Re(1)−N(4) 74.64(15), N(5)−C(20)−C(17) 113.6(5), N(2)−C(9)−C(6) 111.8(4).

combined, decrease the binding affinity of $[BIMB]^{2+}$ and promote decomposition of the NPs under the reaction conditions. In an attempt to delineate the relative contribution of these effects, the electronic and steric properties of the three stabilizers were established. Rhenium carbonyl complexes, $ReCl(CO)_3(N\cap N)$, of the three stabilizers were prepared from $ReCl(CO)_5$ and their IR carbonyl stretching frequencies recorded, see the Supporting Information. In comparison to bipy, the carbonyl stretching frequencies of $[BIHB][Tf_2N]_2$ and $[BIMB][Tf_2N]_2$ were shifted to higher wavenumbers, clarifying that both stabilizers are weaker donors. However, the C_7 alkyl chain in $[BIHB][Tf_2N]_2$ dilutes the electron withdrawing effect of the imidazolium moiety considerably (the ν_{CO} frequencies are shifted by ca. 3 cm^{-1}) and, as a result, is electronically similar to bipy, whereas in $[BIMB][Tf_2N]_2$, the ligand is a considerably weaker donor (shifting the ν_{CO} frequencies by as much as 46 cm^{-1}), which probably contributes to the low catalytic activity of the Rh NPs stabilized by this ligand.

Single crystals of $[BIMB]Cl_2$ and the corresponding rhenium complex, $[ReCl(BIMB)(CO)_3][Tf_2N]_2$, were obtained, and their structures were determined by X-ray crystallography, see Figure 3. In the latter, the imidazolium groups are oriented toward the metal (apparently repelling each other); clearly, and assuming the coordination to a metal surface is similar to that of a homogeneous complex, such a conformation on the Rh NPs would impose a significant hindrance on the catalytic sites. Although it was not possible to obtain a crystal structure of $[BIHB][Tf_2N]_2$, or of the corresponding Re complex, it can be envisaged that the alkyl chain disperses the imidazolium groups away from the metal surface while still providing a slightly greater steric demand than bipy, which might partially account for the greater catalytic activity of the corresponding Rh NPs.

It cannot be ruled out that the imidazolium group can also interact with the NP surface,[15] but evidence for such interactions was not observed. Moreover, at the Rh/ligand ratio used, all coordination sites were blocked, as determined by CO adsorption experiments (see the Supporting Information), which indicates that ligand dissociation is a prerequisite for the catalytic activity.

To determine the leaching of Rh, representative ether extractions from catalytic experiments involving $[BIHB][Tf_2N]_2$ and bipy were analyzed by ICP-MS, revealing that $< 0.1\%$ of the initial Rh in the IL is leached. The retention of the stabilizers within the IL phase was evaluated by ^1H NMR spectroscopy on ether extracts. The amount of leached bipy from the IL phase corresponded to ca. 1.4% of the initial amount, whereas extraction of $[BIHB]^{2+}$ was not detected.

In conclusion, Rh NPs capped with a novel functionalized ligand, $[BIHB][Tf_2N]_2$, exhibit high catalytic activity in arene hydrogenation reactions. Attempts to correlate the differences in activity to the steric and electronic properties of the ligands were also made.

Acknowledgment. We thank the Swiss National Science Foundation (R.R.D.) and the Marie Curie International Incoming Fellowship within the seventh European Community Framework Program project 252125-TCPBRC-BDP (N.Y.) and the EPFL for financial support.

Supporting Information Available: All experimental details including compound synthesis and characterization, X-ray crystallographic data in CIF format, as well as various figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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